RUNOFF AND LEACHING OF SIMAZINE AND DIURON USED ON HIGHWAY RIGHTS-OF-WAY

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March 1996

ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
1020 N Street, Sacramento, California 95814-5624

EH 96-03

EXECUTIVE SUMMARY
of Report EH 96-03 Entitled
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Used on Highway Rights-of-Way

Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulation

PURPOSE

Simazine and diuron are herbicides that have been found in surface and ground water in California. Because they have traditionally been used on highway rights-of-way during the rainy season, this is a potential source of surface and ground water pollution. The Department of Pesticide Regulation (DPR), which is responsible for preventing pesticide contamination of surface and ground water, conducted a study in Glenn County in California's northern Central Valley, in cooperation with the California Department of Transportation (Caltrans), the agency responsible for weed control along all State and interstate highways in California.

STUDY METHODS

Simazine and diuron were applied together in a spray to a 2.4 meter wide strip next to the highway pavement at three sites, and simulated rain was applied to the treated areas. Investigators then measured concentrations of simazine and diuron in water running off the experimental sites, and in soil cores. Similar measurements were made at other treated sites after natural rainfall events.

RESULTS

Where artificial rainfall ran off sites, simazine and diuron were detected in the runoff waters. Simazine concentrations in runoff from sites with artificial rainfall ranged from 78 to 574 parts per billion (ppb). For reference, the U.S. Environmental Protection Agency (US EPA) health advisory for simazine is 4 ppb, which is the same as the Maximum Contaminant Level (MCL) established by the California Department of Health Services (DHS). Diuron concentrations ranged from 144 to 1770 ppb. The US EPA health advisory for diuron is 10 ppb. DHS has not established an MCL for this herbicide. Where natural rainfall ran off sites, simazine and diuron were also detected in the runoff waters. Concentrations ranged from 29 to 337 ppb simazine, and 46 to 2849 ppb diuron.

Soil samples taken at sites receiving artificial rainfall contained simazine and diuron residues both before and after experimental application of these herbicides. Before application, residues in soil ranged from none detected to 694 micrograms simazine per kilogram of soil, and none detected to 145 micrograms diuron per kilogram of soil. Immediately after application, residues ranged from 6.7 to 104 micrograms simazine per kilogram of soil, and 57 to 874 micrograms diuron per kilogram of soil. The high degree of variability of soil residues is probably attributable to the complex infiltration and transport processes in soils. After approximately 321 mm of total seasonal precipitation, residues per kilogram of soil were greatly reduced, to 57 micrograms simazine and up to 94 micrograms diuron. The maximum depth at which herbicide was found at any of the 3 sites was 0.3 m.

Natural rain runoff from one quadrant of a freeway interchange was also sampled during several storms. Only simazine was applied at this site. Samples were collected from a flume that discharged runoff into a drainage canal, which flows through the Sacramento National Wildlife Refuge. Simazine concentrations averaged 105 ppb after 100 mm of rain had fallen, and 83 ppb after the heaviest rainfall sampled.

CONCLUSIONS

During the time that they were cooperating in this study, Caltrans was also in the process of adopting an integrated vegetation management program designed to reduce its use of chemical pesticides for vegetation management. As a result of this program, adopted in 1992, Caltrans has changed the way it manages weeds along rights-of-way. A vegetation management strategy is identified for each treatment site that is as self-sustaining as possible over the long term. Control actions are selected for the near-term which reduce dependence on chemical pesticides. Naturally occurring controls on pests are used where feasible. Because the vegetation management strategy leads to reduced-risk pest management practices, it is consistent with the Department of Pesticide Regulation's pest management strategy, one element of which is to encourage pesticide users to adopt reduced-risk pest management practices.

Where highway treatment sites do receive applications of simazine and diuron, the results of this study indicate that further research is desirable, especially to assess the potential hazard to aquatic life in surface waters receiving runoff from rights-of-way.

ABSTRACT

Simazine and diuron runoff from highway rights-of-way in California is a potential source of environmental contamination because these preemergence herbicides are widely used during the rainy season from November to March. A study to investigate this concern was conducted in Glenn County in California's northern Central Valley, in cooperation with the California Department of Transportation, which is responsible for weed control along all State and Interstate highways. Simazine and diuron were applied together in a spray to a 2.4-m-wide strip next to the highway pavement, at the rate of 2.02 kg simazine active ingredient ha^{-1} and 3.59 kg diuron ha^{-1}. Concentrations of simazine and diuron in highway runoff were measured during both simulated and natural rainfall. Simulated rain (13 mm in 1 hr) was applied to plots on treated highway shoulders at three sites. At one site, none of the artificial rainfall ran off the plot. At the other two sites, 5-12% and 17-46% of the applied water ran off. Simazine concentrations in runoff at these two sites, respectively, ranged from 78-447 and from154-574 $\mu g\ L^{-1}$; diuron concentrations ranged from 144-1175 and 348-1770 $\mu g\ L^{-1}$. Total mass of herbicide leaving the plots in runoff accounted for 0.2-1.8% and 1.6-2.3% of total simazine applied at each of the two sites, respectively, and for 0.2-3.2% and 2.5-5.4% of the diuron. Soil was sampled to a depth of 3 m at the site where no runoff occurred, and to 1 m at the other sites. Soil was sampled to a depth of 3 m at the site where no runoff occurred, and to 1 m at the other sites. Herbicide was not found below 0.3 m depth at any of the 3 sites. Of the total 38 samples taken from the top 0.3 m of soil, 13 contained simazine (maximum concentration 694 ug kg^{-1}, found prior to herbicide application) and 17 contained diuron (maximum concentration 874 ug kg^{-1}, just after rainfall simulation). Natural rain runoff was sampled at a fourth site during several winter storms. Concentrations ranged from 29-337 $\mu g\ L^{-1}$ simazine and 46-2849 $\mu g\ L^{-1}$ diuron. The largest amounts removed in any sampled period were 5.3% of the applied simazine and 8.4% of the diuron in one 28-hr period. Natural runoff from one quadrant of a freeway interchange was also sampled during several storms. Only simazine was applied at this site. Samples were collected from a flume that discharged runoff into a drainage canal. The first runoff sample was taken after a total of 100 mm of rain had fallen, and simazine concentration averaged 105 $\mu g\ L^{-1}$ in 52-66 m^3 of runoff water collected. The greatest mass discharge in any sampled period was 155-200 m^3 of runoff in 20 hr, with an average concentration of 83 $\mu g\ L^{-1}$ simazine. Further research should assess the potential hazard to aquatic life in receiving waters.

ACKNOWLEDGEMENTS

This study would not have been possible without the cooperation and help of the California Department of Transportation (Caltrans). We especially thank Duane Scheurer and Roger Miles of Caltrans District 3 for their extensive help in providing information on Caltrans operations, locating study sites, arranging special herbicide applications, and in general providing the logistical support that made the study possible. We also thank the staff of the District 3 Maintenance Station in Chico, especially Bill Bailey and Steve Caldera, for making the special herbicide applications and for providing detailed information on regular applications. We acknowledge the support of the chemists at CDFA Chemistry Laboratory Services, particularly our primary chemist, Duc Tran, who developed the method for analysis of herbicide deposition samples for this study. Cindy Garretson did the soil texture analyses at the Environmental Monitoring and Pest Management Branch soils laboratory in Fresno. Preparation of sampling materials, the rainfall simulations, sample collection and sample tracking were all carried out by the field staff of the Environmental Hazards Assessment Program, who also assisted in the design, construction and testing of the rain simulation and sampling equipment.

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I. INTRODUCTION

Herbicides are used to control vegetation on California rights-of-way (ROW) by state and county agencies, irrigation and water districts, railroad companies and private landowners. The California Department of Transportation (Caltrans) is responsible for vegetation control on state and interstate highway ROW.

A wide variety of herbicide active ingredients (ai) is used by Caltrans in its ROW maintenance program. The herbicide that is most extensively used in all Caltrans maintenance districts, in terms of pounds of ai applied, is the contact herbicide glyphosate. Following glyphosate in total pounds of ai are the preemergence herbicides simazine and diuron. Other herbicides used extensively are chlorsulfuron, sulfometuron-methyl, oxadiazon, oryzalin and oxyfluorfen (Caltrans, 1991b, 1992). Of these, the preemergence herbicides simazine and diuron have been detected in well water in California (Maes et al., 1992).

The application of preemergence herbicides to highway ROW occurs primarily during the rainy season, the months of October through March, whereas contact herbicides are applied during the dry months (Caltrans, 1991, personal communication). As a result, the highest concentrations of preemergence herbicides are present at a time when rain events occur, creating the potential for these herbicides to be leached deeply into the soil or carried from application sites in storm runoff. In addition, the design of ROW drainage may enhance the possibility that herbicides carried in storm runoff will enter ground or surface waters. For example, highway roadbeds are usually sloped to facilitate the drainage of rainwater away from the pavement, thus causing it to flow over the treated shoulders. Where natural drainage in the immediate vicinity is inadequate, runoff is channeled away from the roadside and toward surface water bodies, or to infiltration areas such as basins and trenches where it is dispersed by evaporation and infiltration. In some basins infiltration may be enhanced by the construction of dry wells, which may act as conduits from the surface to ground water below. It is evident then that the presence of preemergence herbicides in runoff water would increase the potential for their reaching ground or surface water.

Transportation departments in several states, including California, have studied nonpesticide pollutants in highway storm runoff extensively (e.g. Driscoll et al., 1990; Hoffman et al., 1985; Mar et al., 1982, Racin et al., 1982), but there is no evidence in the literature that the presence of pesticides in highway runoff has been examined. The objective of this study was to investigate the movement of simazine and diuron from treated highway ROW in storm runoff.

Glenn County, CA (Fig. 1) was selected as the study location because five herbicides (simazine, diuron, atrazine, prometon and bentazon) had been detected in well water in that area (Cardozo et al., 1989). Figure 2 shows the sections in Glenn County with confirmed detections of simazine or diuron in ground water between the years 1985 and 1990 (CalEPA, 1992). Highway runoff could be one of the mechanisms by which these herbicides were transported from their application sites to ground water.

II. OBJECTIVES

1. Determine what amount of the simazine and diuron that is applied to highway shoulders leaves the treated shoulder in storm runoff, and to what depth it infiltrates the soil on treated shoulders.
2. Determine whether simazine and diuron are contained in highway storm runoff entering Glenn County surface waters.
3. Determine whether simazine and diuron are moving down through the soil in infiltration drainage areas.

III. MATERIALS AND METHODS

Nine study sites were selected. To address Objective 1, rainfall simulation was carried out at Sites 1, 2 and 3, and storm runoff captured at Site 8. Objective 2 was addressed by capturing storm runoff at Site 9. Soil coring was conducted at Sites 4 - 7 to address Objective 3. Tables 1a and 1b summarize the characteristics and Fig. 3 shows the location of each site.

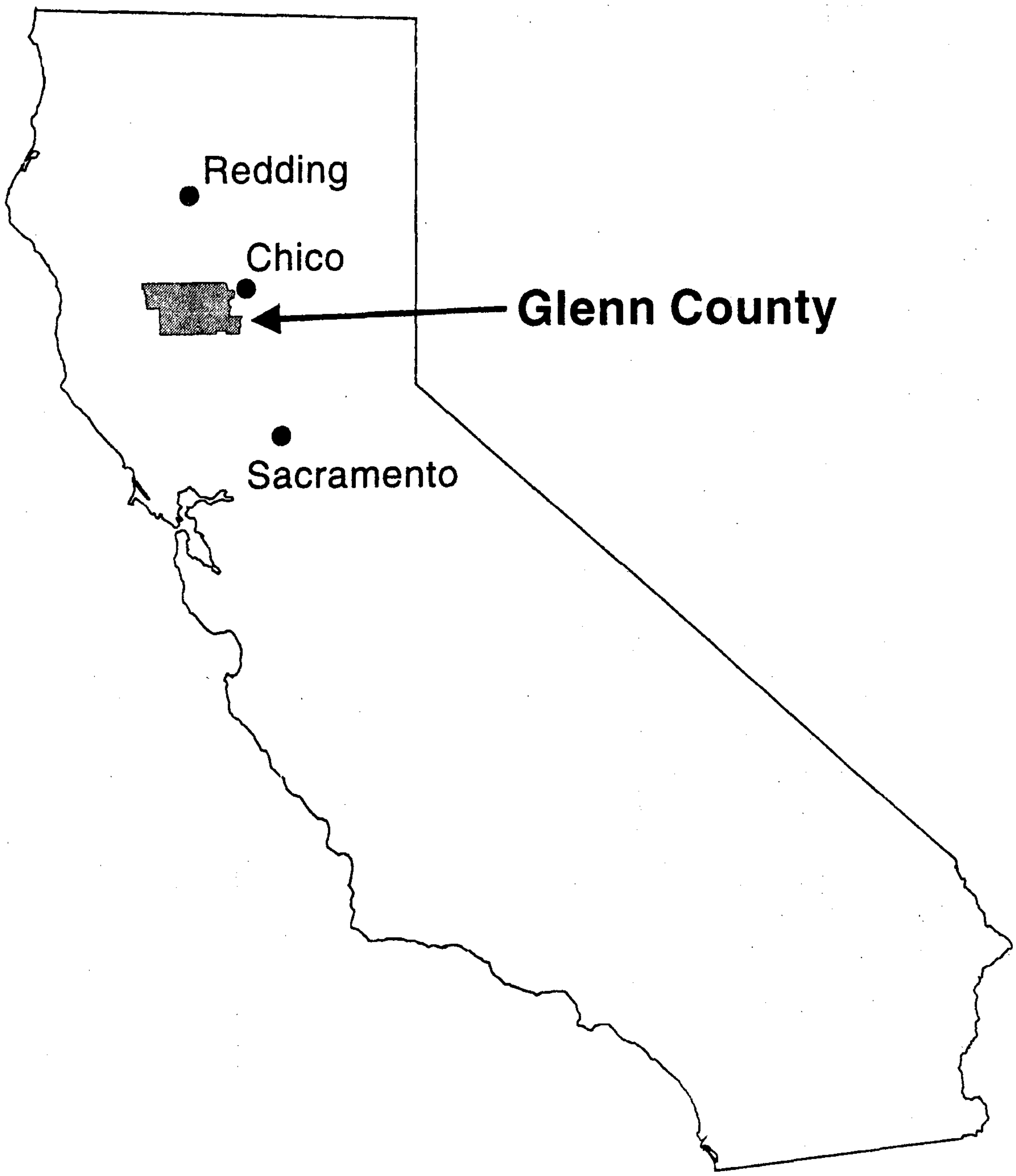

Fig. 1. Location of Glenn County, California.

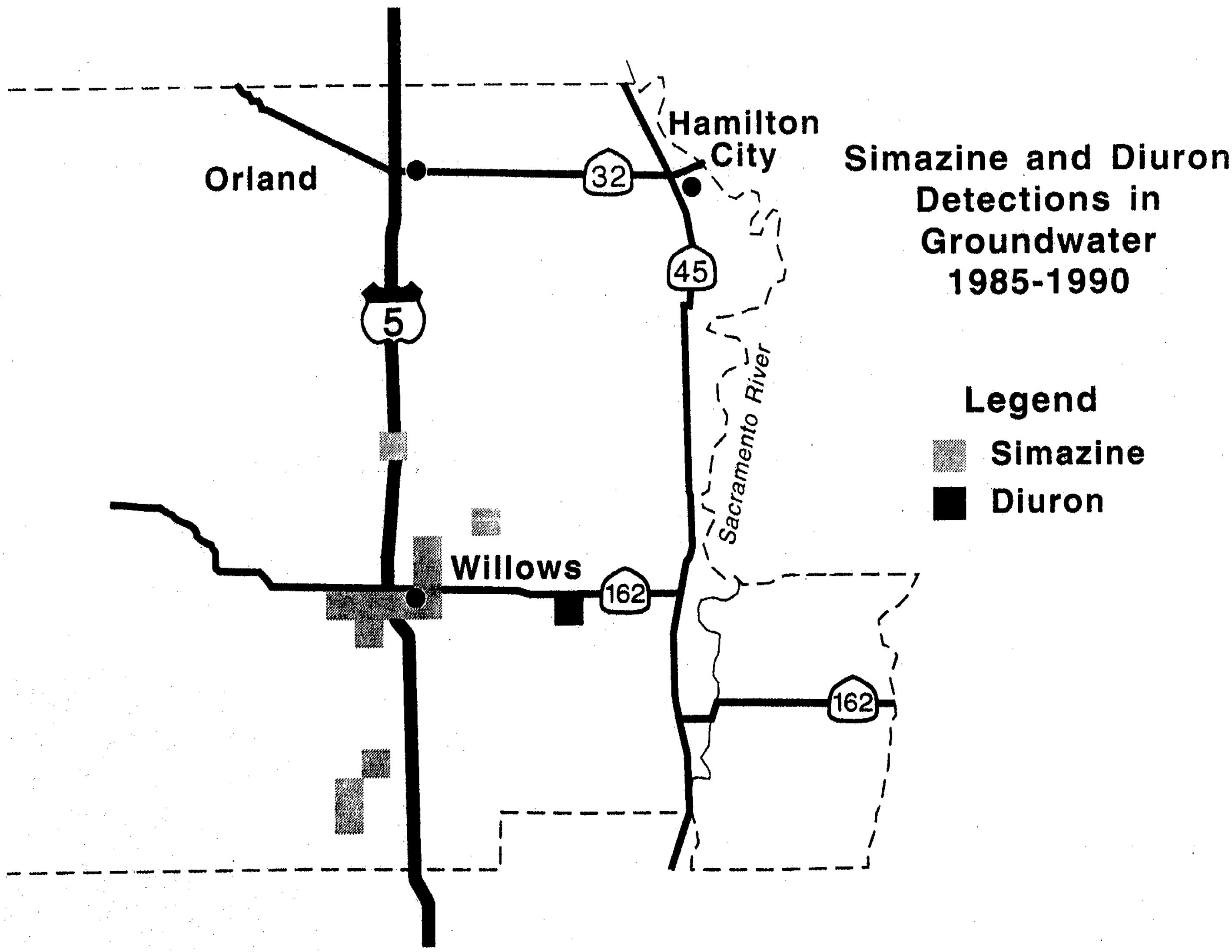

Fig. 2. Locations of Pesticide Management Zones (PMZ) in Glenn County where simazine or diuron was detected in ground water between the years 1985 and 1990 (CalEPA, 1992).

Table 1a. Description of study sites.

Site No.	Highway Location	km (mi)	Other locational Information	Slope of Shoulder	Soil Type[a]
Rainfall simulation sites					
1	32 eastbound	7.2 (4.5)	Rd. RR 0.16km (0.1mi) to west	1.4%	Wn
2	45 southbound	29.8 (18.5)	Rd. 28 0.80 km (0.5mi) to south	7.8%	Tm, Wn, KmA
3	45 southbound	21.7 (13.5)	Ord Ferry Rd. 1.60 km (1mi) north	15.5%	Tm
Infiltration sites (soil coring)					
4	I-5 northbound	2.4 (1.5)	Norman Rd. interchange SE quadrant	-	Rnb
5	I-5 northbound	22.4 (13.9)	Bayliss-Blue Gum Rd. interchange, SE quadrant	-	CaA, MzyA, Av
6	162 eastbound	119.1 (74.0)	Rd. V 0.32 km (0.2mi) to west	-	Pha
7	45 southbound	10.6 (6.6)	At Rd. 52	-	Zba
Rainstorm runoff sites					
8	45 southbound	21.4 (13.25)	Ord Ferry Rd. 2.01 km (1.25mi) north	14.0%	Tm
9	I-5 southbound	12.4 (7.7)	Rd. 57 interchange, NW quadrant	-	Wca, Wcc

[a] From USDA (1968) Soil Survey Maps. Wn = Wyo silt loam; Tm = Tehama silt loam; KmA = Kimball gravelly loam; Rnb = Riz silty clay loam; CaA = Capay clay; MzyA = Myers clay loam; Av = Artois gravelly loam; Pha = Plaza silt loam, dense subsoil; Zba = Zamora silty clay loam; Wca and Wcc = Willows clay.

Table 1b. Description of herbicide treatments to the study sites.

Site No.	Treatment	Application Rates	Application Dates	Sampling Dates	Vegetation
Rainfall simulation sites					
1, 2 and 3	Princep®(shoulder)[a] Karmex®(shoulder)[a]	2.02 kg simazine ai ha^{-1} 3.59 kg diuron ai ha^{-1}	9/24, 25 and 26, respectively	9/24 - 11/8	None
Infiltration sites (soil coring)					
4	Princep (ramps)[b] Krovar® (median)[c]	4.03 kg simazine ai ha^{-1} 2.24 kg diuron ai ha^{-1}	12/9, 11 12/10	12/18 and 6/16	Wild grasses and bare soil
5	Princep (ramps)[b] Krovar (median)[c]	4.03 kg simazine ai ha^{-1} 2.24 kg diuron ai ha^{-1}	12/6-11 1/13	12/18 and 4/6	Eucalyptus and grasses
6	Krovar (shoulder)[d]	2.24 kg diuron ai ha^{-1}	12/9	12/19 and 6/16	Low plants and grasses
7	Princep (shoulder)[a] Karmex (shoulder)[a]	2.02 kg simazine ai ha^{-1} 3.59 kg diuron ai ha^{-1}	1/13-16	12/19 and 4/6	Ditch vegetation
Rainstorm runoff sites					
8[d]	Princep[a] Karmex[a]	2.02 kg simazine ai ha^{-1} 3.59 kg diuron ai ha^{-1}	1/13-16	2/1 - 4/12	None
9	Princep (ramps)[b]	4.03 kg simazine ai ha^{-1}	12/9, 11	2/1 - 4/12	Grasses

[a] Applied to a 2.4-m (8 ft) swath (1.8 lb. ai simazine $acre^{-1}$; 3.2 lb. ai diuron $acre^{-1}$).
[b] Applied to a 1.2-m (4 ft) swath along the ramps (3.6 lb. $acre^{-1}$).
[c] Applied to 1.2-m (4 ft) swath of median (2 lb. $acre^{-1}$).
[d] Applied to 2.4-m (8-ft) swath of shoulder (2 lb. $acre^{-1}$).

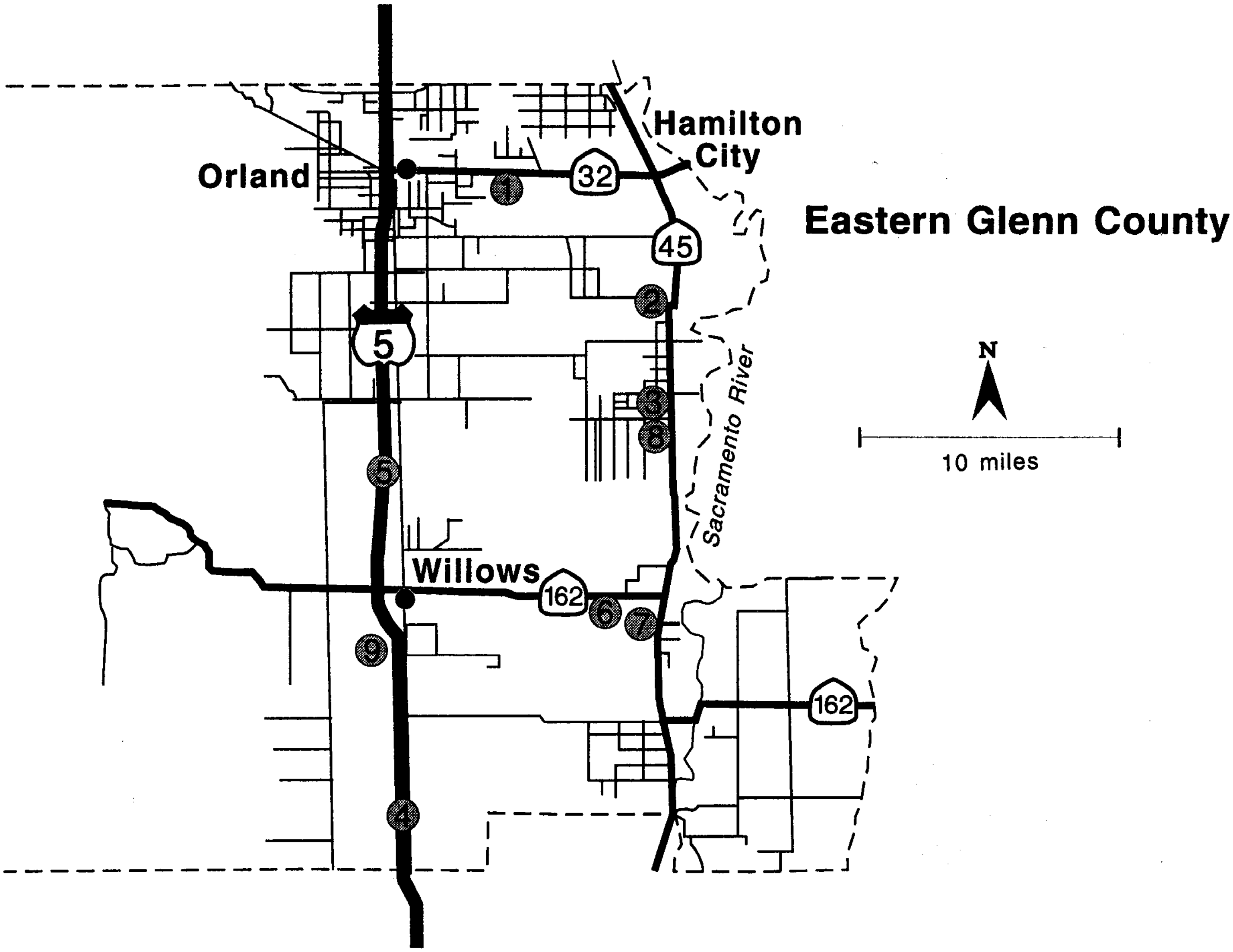

Fig. 3. Locations of study sites in eastern Glenn County.

III.1: Runoff Experiment

A rainfall simulation experiment was designed to measure the movement of simazine and diuron from highway shoulders in storm runoff. Simulated rainfall was applied to treated highway shoulders at intervals of 0, 2 and 4 wk after herbicide application.

Three sites were selected on highways where Caltrans applies simazine and diuron as part of its regular vegetation control program (Fig. 3, Sites 1- 3). The herbicide treatment used here is used extensively by Caltrans statewide. To each mile of highway shoulder is applied a mixture containing 0.9 kg of Princep® Caliber®90 and 1.8 kg of Karmex®, in 190-380 L of water (2.02 kg simazine ai ha^{-1} and 3.59 kg diuron ai ha^{-1}). The spray swath is 2.4 m wide, overlapping the outer 0.3 m of pavement. (In English units this is 2 lb Princep® Caliber®90 and 4 lb Karmex® in 50-100 gallons water (1.8 lb simazine ai ac^{-1} and 3.2 lb diuron ai ac^{-1}) applied to an 8-ft swath overlapping the outer 1 ft of pavement.) Normal applications begin in mid- to late-October, after some rain has moistened the ground. For this study, Caltrans personnel made early applications at the simulation sites in late September to give us time to complete the simulations before real precipitation began. The shoulder at each site was wetted with 13 mm of water the day before herbicide application.

Site 1. Located on the south side of Hwy. 32 (Fig. 3), 8 km west of Hamilton City, the site has wide flat shoulders (1.4 % slope) composed almost exclusively of gravel to a depth greater than 3.0 m (10 ft). Gravel extends at least 7.6 m (25 ft) away from the pavement.

Site 2. Located on the west side of Hwy. 45, 8 km south of Hamilton City (Fig. 3), the site has shoulders of 7.8 % slope. Roadbed gravel extended into one third of each plot, the outer two thirds comprising soil.

Site 3 Located on the west side of Hwy. 45, 16 km south of Hamilton City (Fig. 3), the site has shoulders of 15.5 % slope. Roadbed gravel extended halfway into the plots, the outer half being comprised of soil.

Each site consisted of approximately 22 m of shoulder along one side of the highway, which we divided into four 2.1-m wide and 5.2-m long runoff plots, perpendicular to the road and spaced an average of 4.6 meters apart (Fig. 4). The top of each runoff plot was 0.30 m from the edge of the pavement. Although not ideal, it was necessary for safety to leave this gap between the plots and the road. At Site 3 the plots were only 4.6 m long because space was limited by corn planted close to the road. At each site, three of the four plots were used in the study, the fourth plot being a backup. One additional plot, set up at Site 3 outside the early-spray area, was used to collect background runoff from rain simulated in late October, prior to the regular herbicide application.

Plastic-backed absorbent paper deposition sheets, called "Kimbies", were used to measure herbicide deposition during application. The rectangular 0.093-m^2 Kimbies were attached to plastic-covered squares of cardboard backing, which were placed on the ground and secured in position immediately prior to the herbicide application. At each site, three deposition sheets were placed at equal intervals along a line perpendicular to the pavement between the first two plots (Fig. 4). A second line of sheets was placed between the third and fourth plots. Twenty minutes after the application, the sheets were removed from the cardboard backing, folded and wrapped in aluminum foil, sealed in manila envelopes, and placed on dry ice for transport to the laboratory.

Simulated rain was applied to one plot at each site the day after herbicide application (0 wk). A second plot at each site received simulated rain 2 weeks after herbicide application, and a third plot at each site received simulated rain 4 weeks after the application. Every plot received a second simulated rain 2 weeks after its first. This allowed sampling of runoff from rain at different lengths of time after herbicide application, and from first and second rainfalls..

Rainfall was simulated for one hour at the rate of 13 mm h^{-1}. This intensity was chosen to represent a heavy but not extremely unusual rainfall for the region, based on rainfall intensity-duration-frequency curves for Red Bluff, CA, 51 km north of the study area (US. Dept. of Commerce Weather Bureau, 1955). The curves indicate that every two years, on average, a

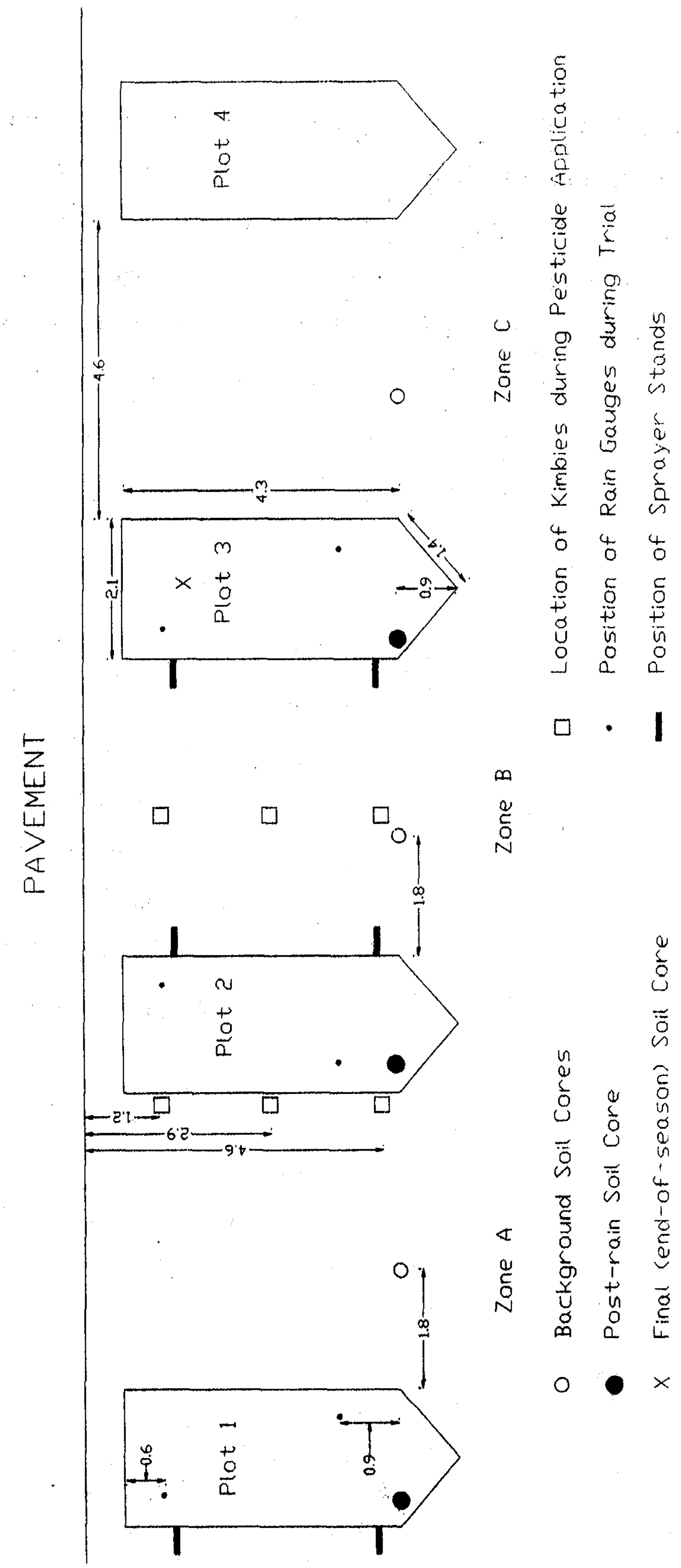

Fig. 4. Generic site diagram of plots and sampling locations at Sites 1, 2 and 3 (in meters)

storm event with 1-hr rainfall intensities of at least 16.5 mm hr^{-1} and 2-hr rainfall intensities of at least 11.4 mm hr^{-1} is expected to occur in this region. The 1-hr simulation duration was chosen for convenience. Rainfall was applied with two Spraying Systems Co. 1/4 HH14WSQ Fulljet nozzles, mounted above the centerline of the plot (Fig. 4). The nozzles were operated according to the specifications of Bubenzer et al. (1985, 1991) and Molnau (1991), who reported that they produced drop size distributions and drop impact velocities similar to storms with rainfall intensities of 2.5 to 10 mm hr^{-1}. These intensities are similar to winter storms in northern California. Other nozzles that have typically been used in rainfall simulation produce drop characteristics similar to much higher-intensity rainfall (Shelton et al., 1985). To achieve the intensity of 13 mm of rain in 1 hour, each nozzle cycled on for 15 seconds and off for 45 seconds.

In addition to overhead rainfall simulation, a 'pavement simulator' was used to simulate runoff from the paved roadbed that would run over the shoulder, diluting pesticide concentrations in the shoulder runoff itself. It was assumed that rain falling from the centerline to the edge of the road would run off over the shoulder. The volume of pavement runoff was estimated to be 80 % of the simulated rainfall of 13 mm, from an area half the width of the road by the width of the plot (3.6 m by 2.1 m). The runoff coefficient of 0.80, representing the portion of rainfall that runs off, was chosen based on data for asphalt pavements (Johnson and Chang, 1984). The volume thus estimated was 80 L. The pavement simulator consisted a 2.1-m-long perforated PVC pipe held horizontally just above the ground on the upper (closest to the highway) border of the plot. At 0.083-h (5-min) intervals throughout the duration of the simulation, equal portions of the 80-L total were poured into the perforated pipe, which dispersed the water evenly across the width of the plot.

All water running off the plot was captured, and composite samples of the runoff taken for chemical analysis. To collect runoff from a plot, runoff was channeled to a collection point by sheet metal barriers that were pounded into the ground along the sides of the plot and in a V shape at the bottom of the plot (Fig. 4). Runoff flowed through a 0.76-m opening at the vertex of the V over a sheet of Teflon film, into a stainless steel bowl placed in a hole in the ground. The

Teflon sheet was sealed to the ground with silicone caulk diluted with mineral spirits (Wauchope, 1991, personal communication). As runoff collected in the stainless steel bowl, it was transferred to a large galvanized steel can using a glass cup. The person doing this wore latex gloves to avoid contaminating the samples.

When runoff stopped, the collected runoff water was mixed thoroughly in the galvanized container and two 1-L samples were collected by immersing amber glass bottles. The samples were put on wet ice for transport to the laboratory. After the samples were taken, the volume of remaining runoff was measured. After each simulation, all equipment was washed with soapy water and rinsed with deionized water. In addition, trowels, spatulas, scissors, collector bowls, glass cups and galvanized cans were rinsed with isopropyl alcohol.

Soil cores were taken at the simulation sites three times: (1) in September, just before the herbicide application, to determine background concentrations, (2) in November after the completion of the last rainfall simulation, and (3) in April at the end of the rainy season. Three 0.9-m-deep background cores were taken at each site except Site 1, where overhead wires permitted taking only two. Background coring locations were about 4.5 m from the edge of the pavement, between the runoff plots (locations shown in Fig. 4). After the simulations, three 0.9-m-deep cores at Sites 2 and 3, and two 3.0-m cores at Site 1 (as explained in the results section), were taken in each runoff plot 4.3 to 4.5 m from the pavement (Fig. 4). At the end of the season, one 3.0-m core was taken at each site, 1.8 m from the pavement in one of the runoff plots (Fig. 4).

Cores were obtained using a 0.45-m split-barrel sampler holding three 15-cm stainless steel tubes (inner diameter 6 cm), inserted into the auger of a motorized drilling rig. The upper 0.30 m of each core was sampled in 0.15-m increments, the remainder in 0.30-m increments. For each increment, the soil was removed from the cylinder(s) and mixed in a plastic bag to a homogeneous sample. A 0.5 L Mason jar was filled with the mixed soil, transported on dry ice, and stored frozen until chemical analysis. A 150-g portion of each increment of the first core taken at a site was kept for textural analysis. It was placed in a 200 by 300-mm plastic bag that was left open overnight to allow partial drying of the soil before being sealed and transported to the Department of Pesticide Regulation (DPR) Environmental Monitoring Branch soils laboratory in Fresno.

Site 8. Located on the west side of Hwy. 45, 16.5 km south of Hamilton City and 0.4 km south of Site 3 (Fig. 3), the site has shoulders of 14.0 % slope and soil essentially identical to that at Site 3. Two plots of similar construction to those used at the simulated rainfall sites were installed on the highway shoulder to collect storm runoff. The same treatment given the simulation sites in September was applied at Site 8 in January 1992, as part of the normal Caltrans treatment program. As in the simulations, runoff was collected at the bottom of the plot in a stainless steel bowl and transferred to a galvanized steel can. Whenever 40 L of runoff had collected in the can, the contents were stirred thoroughly and two 1-L amber bottles filled by submersion. The galvanized can was then emptied, rinsed with deionized water and alcohol, and runoff collection continued. Samples were stored on wet ice during transport to the laboratory. Runoff from the highway shoulder was collected at this site during four rainfall events that occurred during the months of February and April, 1992.

III.2: Discharge of Runoff to Surface Water

In some places, runoff from highways is discharged directly into an active stream course or other surface water body. Frequently, the same ditch is used for agricultural drainage, so the presence of pesticides in the ditch water cannot be attributed entirely to highway runoff. A site was found where runoff could be sampled as it left a freeway interchange before being discharged into a surface canal.

Site 9. Located in the northeast quadrant of the I-5 and County Road 57 interchange, 3.2 km south of Willows (Fig. 3). The northeast quadrant is divided by ramps into a circular and a triangular section (Fig. 5). It is drained by an open ditch that traverses both sections of the quadrant, passes under the outer ramp through a culvert and runs down an asphalt-lined channel

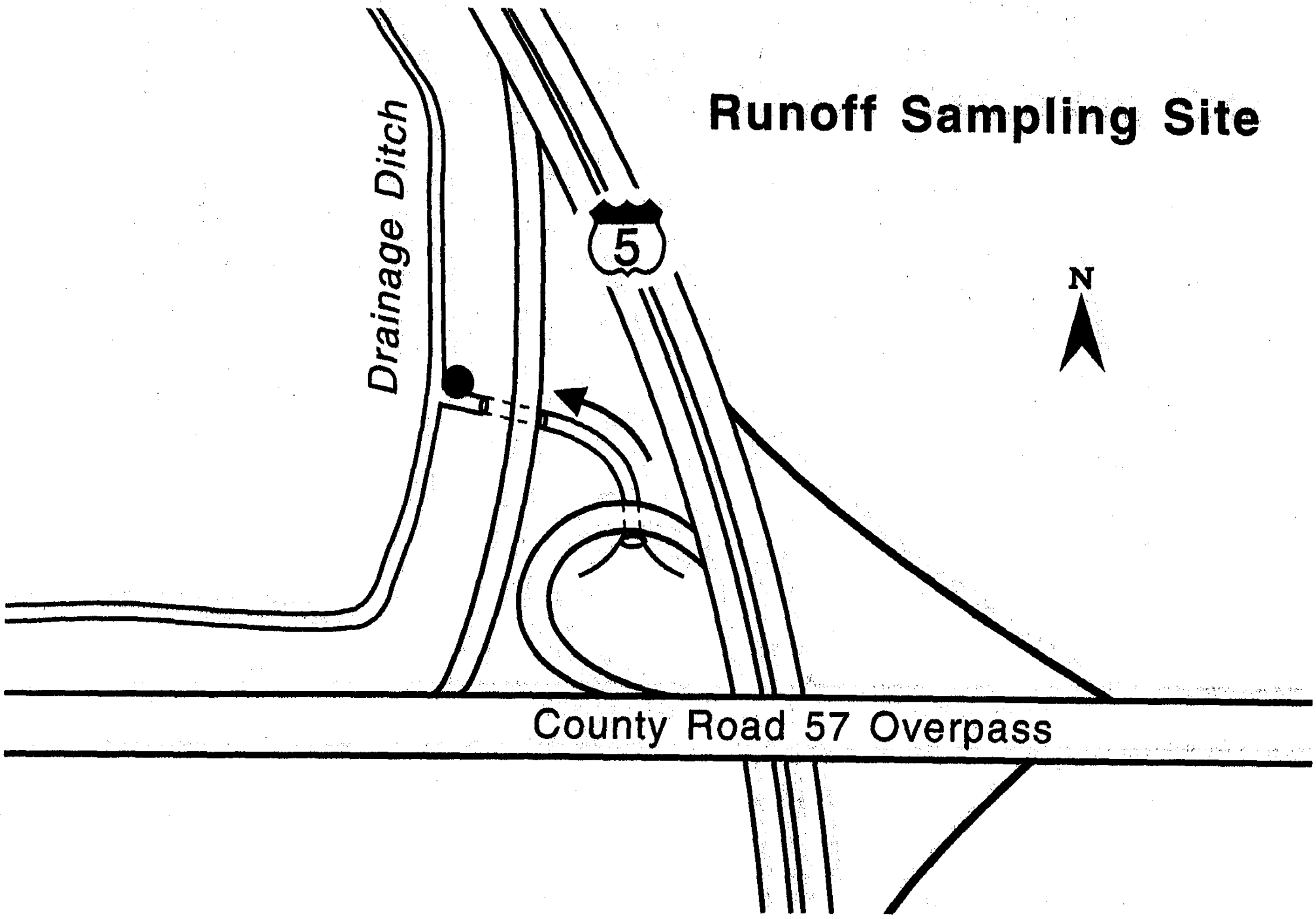

Fig. 5. Site 9, showing the location of the flow-splitting sampler.

into a drainage ditch. The ditch water flows through a county drain into the Sacramento National Wildlife Refuge, where it may flow through a network of creeks draining into the Colusa Drain and, ultimately, the Sacramento River. The size of the area contributing runoff was estimated to be 1.9 hectares, of which 33 % is paved. Area was estimated from Caltrans' engineering drawings of the site, obtained from the regional maintenance office in Chico, CA. The unpaved area, with the exception of roadway shoulders, is vegetated by grasses. Simazine was applied to a 1.2-m swath along the ramps in December 1991 at the rate of 4.03 kg simazine ai ha^{-1}. The treated area represents 3.1 % (0.06 ha) of the total drainage area.

A flow-splitting sampler, constructed according to the design of Clark and Mar (1980), was installed at Site 9 and all runoff discharged from the quadrant diverted through the sampler. The flow-splitter was chosen to satisfy a number of criteria, including the ability to 1) operate without a power source, 2) collect runoff samples unattended, and 3) be left on site with minimal risk of theft or vandalism. The flow-splitter consists of a rectangular open-channel steel flume that directs a stream of water through a series of baffles, which split the flow into progressively smaller fractions (Fig. 6). The final fraction is diverted into a collection vessel, providing a volume-weighted composite sample of the total flow. Our flow-splitter was built to capture 1.0 % of the total flow volume. In tests conducted by Clark and Mar (1980), the actual capture rate of a 1.0 % flow-splitter was 1.2 ± 0.15 %.

Runoff was collected during four precipitation events during the months of February and March, 1992. Herbicide discharge into the drainage ditch was estimated from the measured total volume of water collected during the precipitation events and the herbicide concentration of the discharge.

III.3: Leaching beneath Infiltration Areas

The third objective was addressed by taking soil cores at the beginning and end of the rainy season at four sites where runoff water either flows over the soil or is detained for infiltration into

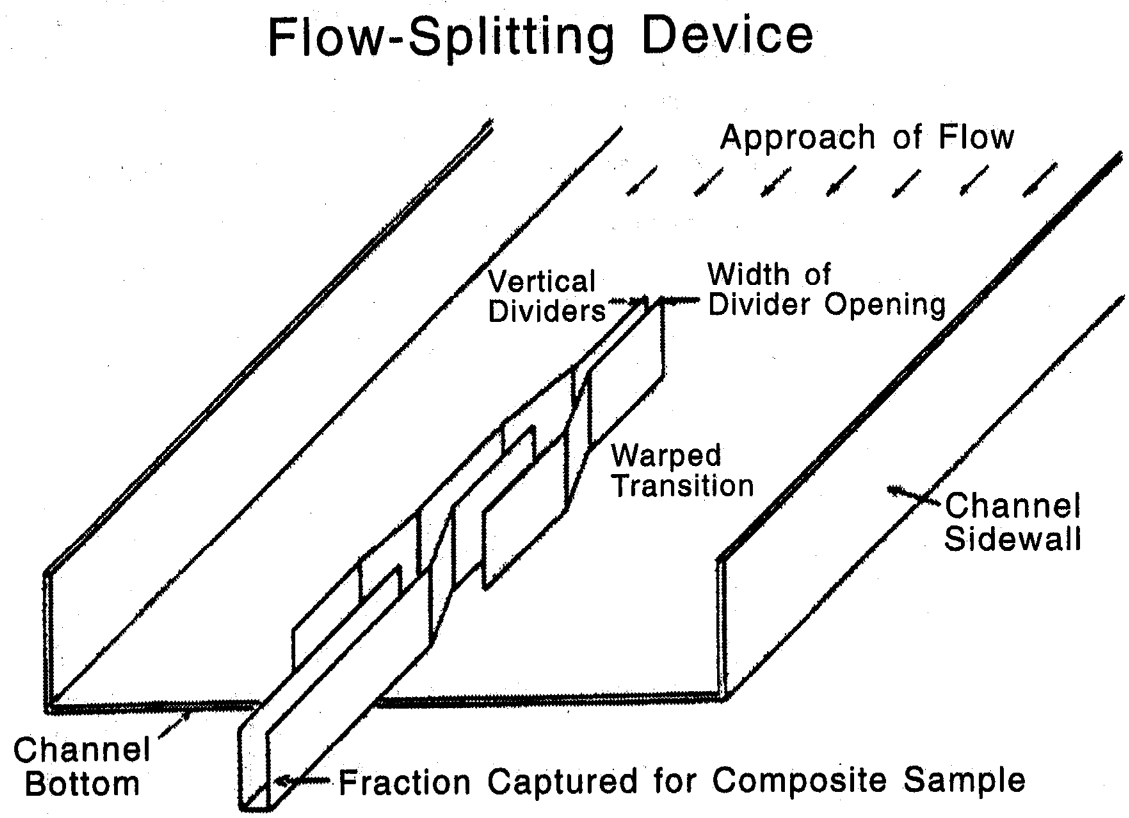

Fig. 6. Diagrammatic representation of the flow-splitting device adapted from a design of Clark and Mar (1980).

the soil. One 3.0-m core was taken at each site just before or after Caltrans' fall application of simazine and diuron (December 1991), and another at the end of the rainy season (April 1992). As in the simulated rainfall study, the top 0.30 m of soil was sampled in 0.15-m increments, the remainder in 0.30-m increments. Similarly, the first core taken at each site was split for soil textural analysis.

Site 4. Southeast quadrant of the I-5 and Norman Road (Rd 68) interchange, 2.4 km north of the Colusa County line (Fig. 3). The northeast quadrant and the median drain into the southeast quadrant, which in turn drains through an open ditch to a culvert that channels the water out of the interchange. Vegetation cover is predominantly wild grasses. Some areas were bare where the collection of drainage water provided too moist an environment for grass. Caltrans applied 4.03 kg simazine ai ha^{-1} (3.6 lb. $acre^{-1}$) to a 1.2-m (4-ft) swath along the ramps, and 2.24 kg diuron ai ha^{-1} (2 lb. $acre^{-1}$) to a 1.2-m swath of median in December of 1991. Soil cores were taken in a depression near the entrance to the culvert, where the recent presence of water was apparent. The coring location was at least 6 m from any areas that receive herbicide applications. In December, the soil was wet throughout the 3.0-m core sample, and in April 1992 the area was under water, preventing the collection of soil cores. During coring in June 1992, the soil was wet and ground water was encountered at a depth of 1.5 m (5 ft).

Site 5. Southeast quadrant of the I-5 and Bayliss-Blue Gum Road interchange, 6.4 km north of Willows (Fig. 3). The quadrant is divided by ramps into two sections, one circular and one triangular. The circular section was chosen for coring because it is drained by an open ditch that channels runoff across the section and through a culvert out of the interchange. At the time of the study there was no water in the ditch. Vegetation includes a stand of eucalyptus and some grasses, although the soil is mostly bare. Caltrans applied 4.03 kg simazine ai ha^{-1} to a 1.2-m swath along the ramps, and 2.24 kg diuron ai ha^{-1} to a 1.2-m swath on the median in December of 1991. Coring was done in the lowest part of the drainage ditch, at least 6 m from areas that receive herbicide applications. Soil cores were taken in December 1991 and April 1992, and at both times the soil was observed to be dry.

Site 6. South side of Hwy. 162, 11.3 km east of Willows (Fig. 3). The terrain slopes unevenly away from the shoulder into an area which may best be described as 'boggy'. Adjacent property is under rice cultivation and is separated from the site by a low levee with a dirt road. Caltrans applied Krovar® (2.24 kg diuron ai ha^{-1} (2 lb. $acre^{-1}$)) to a 2.4-m swath of shoulder in December of 1991. Soil cores were taken 4.5 m from the pavement, thus only 2.4 m from areas which had received herbicide application. The soil cores collected in December were observed to be moist. In April 1992 there was standing water on the site and no soil cores could be taken. Cores taken in June 1992 were wet, and ground water was encountered at 1.8 m.

Site 7. West side of Hwy. 45, 0.8 km south of Glenn (Fig. 3). The shoulder slopes steeply into a narrow ditch running along the highway. A high levee with a dirt road separates the ditch from an agricultural canal paralleling the highway. The same treatment given the simulation sites in September was applied at Site 7 in January 1992, as part of the normal Caltrans treatment program. Cores were taken in the bottom of the ditch about 1.8 m from the road, within the swath that should have received direct herbicide application. The thick vegetation in the ditch, however, suggested that this may have been light.

Additional infiltration soil samples were taken at Sites 1 and 2 in April 1992. These cores were taken in depressions 10 and 7.6 m from the pavement at Sites 1 and 2, respectively.

IV. CHEMICAL ANALYSIS/QUALITY CONTROL

All chemical analyses were performed by the Chemistry Laboratory Services of the California Department of Food and Agriculture (CDFA). Chemical analytical methods are described in Appendix B.

Sediment was filtered from the water samples and analyzed separately. All filtered aqueous samples were analyzed for simazine and diuron using a multipesticide residue analysis developed for the DPR to measure atrazine, bromacil, diuron, prometon and simazine in well water. The method uses solid-phase extraction and gas chromatography with a thermionic specific detector (TSD), and has a detection limit of 0.1 $\mu g\ L^{-1}$ for both chemicals. Results are reported in $\mu g\ L^{-1}$. One matrix blank and one matrix spike were analyzed with each extraction set. Quality Control results are presented in Appendix C.

Soil samples were analyzed for simazine and diuron using a multipesticide screen developed for DPR compliance monitoring. The method uses hexane:acetone followed by solid-phase extraction, and gas chromatography with ultra-violet (UV) detector. It has a detection limit of 4 $\mu g\ kg^{-1}$ for simazine and 40 $\mu g\ kg^{-1}$ for diuron. Results are reported in μg herbicide kg^{-1} dry soil. One matrix blank and one matrix spike were analyzed with each extraction set (Appendix C). The same method was used to determine the concentration of simazine and diuron in the sediment filtered from runoff water.

A method for determining the mass of simazine and diuron on deposition sheets (Kimbies) was developed for this study by the CDFA laboratory. Pesticide residues were extracted from the deposition sheets with methanol and the extract analyzed using both gas and liquid chromatography, with TSD and UV detectors, respectively. The method has a detection limit of 0.0005 mg/sample for both chemicals, where a sample is one 0.093 m^2 deposition sheet. Results are reported in mg/sample. One matrix blank and one matrix spike were analyzed with each extraction set (Appendix C).

V. RESULTS AND DISCUSSION

V.1: Runoff Experiment

V.1.a: Herbicide Application - Average measured deposition of simazine and diuron (in mg/plot) at each site was calculated by first averaging deposition on the two Kimbies at each distance from the pavement (Fig. 4), then calculating a weighted average of the three distances, with deposition at each distance weighted by the fraction of total plot area it represented (because the plots were not rectangular, the sheets at the greatest distance from the pavement represented a smaller fraction of the plot area). Deposition of both simazine and diuron varied considerably between sites (Table 2). *Target* deposition was calculated assuming the 1.8 m (6 ft) of the plot nearest the pavement was sprayed at the nominal application rate of 2.02 kg simazine ai ha^{-1} and 3.59 kg diuron ai ha^{-1}, while the rest of the plot received no spray. Measured deposition of simazine at the three sites ranged from 68 to 102 % of target, and diuron deposition from 58 to 93 % of target. The raw data are presented in Appendix D.

V.1.b. Soil Texture - Each site had distinct soil texture (Appendix E). Site 1 is located in the gravelly alluvial plain of Stony Creek and its soil to 3.0 m was almost entirely gravel and sand. Although the map unit (soil type) indicated for this site on the Soil Conservation Service (SCS) map is Wyo silty loam (USDA, 1968), the soil encountered was more gravelly. It may be that much of the soil is imported roadbed construction material, but the depth and extent of the gravel makes this seem unlikely. Site 2 could not be located precisely on the SCS map but is probably Kimball gravelly loam. Site 2 was intermediate in texture between Sites 1 and 3, having much less gravel and sand than Site 1, but more than Site 3 (Tehama silt loam). Site 3 had more silt and clay than Site 2.

V.1.c. Runoff - No runoff occurred at Site 1, even after simulated rainfall was extended to a duration of two hours (26 mm of rain). This may be attributable to the porosity of the shoulder material, which was predominantly gravel and sand, and to the flatness of the shoulder. After observing the same result on two plots, rain simulation was discontinued at Site 1. Site 2 plots yielded 10 to 25 L of runoff per simulation (Table 3). Runoff at Site 3 measured 30 to 90 L per simulation. The larger amount of runoff at Site 3 was probably due to greater shoulder slope, 15.5% at Site 3 versus 7.8 % at Site 2, and to the differences in soil texture.

Simazine and diuron were detected in all runoff samples (Table 4), at concentrations from 78 to 574 μg simazine L^{-1} runoff, and 144 to 1770 μg diuron L^{-1} runoff. Herbicide concentrations reported in runoff are the sum of the water and sediment components unless otherwise stated. The highest concentrations of each were observed one day after herbicide application, but

Table 2. Measured deposition of simazine and diuron applied at Sites 1, 2 and 3.

Site	Simazine	Diuron
	------------------------mg/plot------------------------	
1	798	1302
2	533	813
3[a]	802	1073
Target Deposition[b]	788	1400

[a] Although plots at Site 3 were 0.6 m (2 ft) shorter than at Sites 1 & 2, the last 0.6 m (2 ft) of the longer plots contributed almost nothing to total mass deposition.

[b] Based on the nominal application rate.

Table 3. Volume of runoff from the rainfall simulation plots, expressed as a total volume and as a percentage of the total water applied.

Weeks after Application	Site 2[a] Plot 1	Site 2[a] Plot 2	Site 2[a] Plot 3	Site 3[b] Plot 1	Site 3[b] Plot 2	Site 3[b] Plot 3
	L (%)					
0	21.8 (10.5)			32.5 (16.7)		
2	24.2 (11.6)	20[c] (9.6)		57.4 (29.4)	45.5 (23.3)	
4		10.5 (5.1)	10.0 (4.8)		90.0 (46.2)	64.5 (33.1)
6			21.8 (10.5)			65.0 (33.3)

Note: no runoff occurred at Site 1.
[a] 207.5 L water applied.
[b] 195 L water applied (Site 3 plots were smaller).
[c] Estimated quantity; no measurement obtained.

Table 4. **Concentration[a] and percent of measured application of simazine and diuron in runoff from the rainfall simulation plots.**

Weeks after Application	Site 2						Site 3					
	Simazine			Diuron			Simazine			Diuron		
	Plot			Plot			Plot			Plot		
	1	2	3	1	2	3	1	2	3	1	2	3
	$\mu g\ L^{-1}$ (%)											
0	447 (1.8)			1175 (3.2)			574 (2.3)			1770 (5.4)		
2	339 (1.5)	82 (0.3)		631 (1.9)	194 (0.5)		275 (2.0)	334 (1.9)		611 (3.3)	1097 (4.7)	
4		115 (0.2)	110 (0.2)		212 (0.3)	144 (0.2)		154 (1.7)	243 (2.0)		348 (2.9)	766 (4.7)
6			78 (0.3)			162 (0.4)			201 (1.6)			419 (2.5)

[a] Concentrations reflect combined water and sediment loads.

residues were still observed in runoff after first rainfalls 4 wk after application, and after second rainfalls. As much as 162 μg simazine L^{-1} and 419 μg diuron L^{-1} were observed in runoff from a second rainfall 6 wk after herbicide application. Even preapplication (background) rainfall simulation produced runoff with some herbicide residue: 5 μg simazine and 13 μg diuron L^{-1} runoff. This represents material still available after a full winter rainy season and a full summer. The percentage of the measured application of herbicide removed in runoff from 1 hr of simulated rain was between 0.2 and 2.3 % of simazine and from 0.2 to 5.4 % of diuron. (These percentages must be interpreted with the small number and large variability of the deposition measurements in mind.) A number of investigators have used simulated rainfall to examine herbicide loss in runoff from agricultural plots (Felsot et al., 1990; Leonard, 1988; Pantone et al., 1992; Wauchope et al., 1990). The percentage of herbicide removed in one rain event ranged from 0.05 - 4.7 % of atrazine (plus one extreme value of 18.3 %, which is discussed below), 0.1 - 8.0 % of alachlor (plus one extreme value of 22.1 %), 0.08 - 3.4 % of cyanazine, 0.4 - 2.3 % of sulfometuron-methyl, 3.0 - 8.0 % of 2,4-D salt, 2.5 - 10.3 % of 2,4-D acid and 26 - 27 % of 2,4-D ester. Like ours, these studies consistently found decreasing loss with time since application. With such a wide range of observed losses, ours are consistent with those found in agriculture in spite of many differences between those studies and ours. (Those studies all used higher-intensity rainfall (from 63 to about 72 mm hr^{-1}) than our 13 mm hr^{-1}, and several used longer rainfall durations (up to 2 hr compared to our 1 hr). The agricultural plots were grass-covered, plowed or planted to crops, while our plots had nearly bare, highly compacted soils.)

Although concentrations of both herbicides in sediment carried in runoff were high, the sediment load was usually light enough that it did not contribute much to the total concentration in runoff. Sediment concentrations ranged from 1.0 to 5.1 μg simazine g^{-1} sediment (mean 3.16 $\mu g\ g^{-1}$), and from 3.6 to 10.4 μg diuron g^{-1} sediment (mean 6.73 $\mu g\ g^{-1}$). The percentage of the total herbicide in runoff contributed by sediment ranged from 0.43 to 17 % of simazine (mean 2.95 %), and from 0.57 to 38 % of diuron (mean 5.04 %). The highest percentages for both simazine and diuron came from one event in which sediment load was exceptionally high; the next highest percentages were 3.3 and 3.0 %, for simazine and diuron, respectively.

Actual rain runoff from treated highway shoulders was captured at Site 8 during rain storms in February and April of 1992. Simazine and diuron were applied to the shoulder between January 13 and 16. Table 5a shows precipitation recorded at the nearest CIMIS stations, Durham and Orland, between the application and the conclusion of this study. Approximately 9 mm of rain had fallen at Site 8 before the first runoff sampling on 1 February. Simazine and diuron were detected in all the runoff samples, with concentrations of both decreasing with time since herbicide application (Table 5b). Simazine concentration decreased from 377 $\mu g\ L^{-1}$ on 1 February to 29 $\mu g\ L^{-1}$ on 12 April, and diuron from 2849 $\mu g\ L^{-1}$ to 4 $\mu g\ L^{-1}$ during the same period. As much as 8.4 % of the target application of diuron was removed during one sampling period. Table 6 compares simazine and diuron in runoff of simulated and actual rainfall, in events with similar conditions. At Sites 2 and 3, one plot received its second simulated rainfall four weeks after herbicide application. Between the application and the second rainfall, 13 mm of artificial rain had been applied. At Site 8, rainfall also occurred four weeks after application, prior to which 25 mm of natural rain had fallen since the application. The simulation data underestimate concentrations in actual runoff by a considerable degree. In fact, the concentrations in actual runoff four weeks after application, with some rain intervening (Table 5b), are very close to those observed in simulated runoff one day after application (Table 4). One reason for the higher values in actual runoff was that runoff from the pavement flowed over the full 2.4-m spray swath, whereas simulated runoff flowed only over the outer 1.8 m of the swath. This can account for only a small part of the difference, however. The discrepancy may arise from a number of additional factors, including the fact that simulation plots were treated in September while Site 8 was treated the following January. In Glenn County there are considerable differences between climatic conditions in September and January, the former being typically sunny, warm or hot and dry, and the latter mostly cloudy, cool and wet. These differences may affect the rates at which the herbicides break down on and in the soil, the physical and chemical characteristics of soils themselves or the proportion of rain that runs off the shoulder.

Table 5a. Precipitation events pertinent to runoff sampling at Site 8 on Hwy 45.

Date (1992)	Recording Location[a]					
	Durham		Orland		mean	
mm/dd	mm (inches)					
1/28	9.9	(0.39)	8.1	(0.32)	9.1	(0.36)
2/1[b]	8.9	(0.35)	14.0	(0.55)	11.4	(0.45)
2/9-15[b]	125.0	(4.92)	112.0	(4.41)	118.4	(4.66)
2/18-19	36.1	(1.42)	38.1	(1.50)	37.1	(1.46)
2/21	8.9	(0.35)	5.6	(0.22)	2.0	(0.08)
3/1	3.0	(0.12)	3.0	(0.12)	3.0	(0.12)
3/5-6	50.5	(1.99)	34.8	(1.37)	42.7	(1.68)
3/14-16	51.1	(2.01)	63.8	(2.51)	57.4	(2.26)
3/22	5.1	(0.20)	11.9	(0.47)	8.6	(0.34)
4/9	3.0	(0.12)	0.0	(0.00)	1.5	(0.06)
4/11-4/12[b]	32.0	(1.26)	21.1	(0.83)	26.4	(1.04)
Total	333.5	(13.13)	312.4	(12.30)	321.3	(12.65)

[a] Data obtained from DWR (CIMIS). Orland, 21 km (13 mi) NW, and Durham, 18 km (11 mi) E, are the two closest CIMIS stations to the site. Data was recorded in inches and converted to millimeters for this report.

[b] Sampling was done during portions of these precipitation events.

Table 5b. Samples of storm runoff collected from the shoulder of Hwy 45 (Site 8) after herbicide application on about 1/14/92[a].

Sampling Date	No. of weeks after spray	Cumulative rainfall[b] between appl. and sampling	Sampling duration	Rainfall[c] during sampling	Runoff during sampling	Pesticide concentration in runoff[d]		Amount of target application removed in runoff during sampling		Percent of rainfall running off
						Simazine	Diuron	Simazine	Diuron	
		mm (in)[e]	hh:mm	mm (in)[e]	L	------μg L^{-1}------		--------%--------		
2/1	2.5	20 (0.8)	6:40	8.1 (0.32)	>46[f]	377	2849	1.6	7.0	30
2/9	4	25 (1.0)	28:00	14.5 (0.57)	>153[f]	362	1027	5.3	8.4	57
2/15	4	84 (3.3)	5:20	23.4 (0.92)	360	49	66	1.6	1.3	83
4/11	13	287 (11.3)	16:00	13.7 (0.54)	>45[f]	29	46	0.12	0.11	18
			Total	59.7 (2.35)				8.6	16.8	

[a] Samples collected from 2 plots and results averaged.
[b] Average of measurements taken at Orland and Durham.
[c] Measured on site.
[d] Volume-weighted mean for the duration of sampling.
[e] Data was recorded in inches and converted to millimeters for this report.
[f] Collectors overflowed at one point during each sampling period, so measured runoff is underestimated by an unknown amount.

Table 6. A comparison of simazine and diruon runoff in simulated[a] and actual[b] rainfall extrapolated to one kilometer of highway (1 side).

	Runoff	Simazine		Diuron	
	m^3	$\mu g\ L^{-1}$	$g\ km^{-1}$	$\mu g\ L^{-1}$	$g\ km^{-1}$
Simulation[a] :					
13 mm rain in 1-h period 4 wk post spray with 13 mm rain preceding	4.9 - 41.8	115 - 154	0.56 - 6.5	212 - 348	1.0 - 14.7
Actual[b] :					
15 mm rain in 28-h period 4 wk post spray with 21 mm rain preceding	> 71	362	> 26	1027	> 73

[a] Ranges defined by Site 2 and Site 3, September and October, 1991.
[b] Site 8 on 9 February 1992.

V.1.d. Soil Coring at Simulation Sites - Soil was sampled to 0.90 m in September 1991, prior to the herbicide application. No residues were detected at Site 1. However, both simazine and diuron were detected in the first 0.30 m at Sites 2 and 3 (Tables 7a and 7b), at concentrations ranging from none detected (ND) to 694 μg simazine kg^{-1} soil and ND to 145 μg diuron kg^{-1} soil. (The value of 694 μg simazine kg^{-1} soil is difficult to explain. It may reflect true nonuniformity of application, but it is highly aberrant.)

The second set of soil cores was sampled in November 1991 after the final rainfall simulation. Because no runoff occurred at Site 1, soil cores there were taken to a depth of 3.0 m in order to look for deeper infiltration of herbicide. Soil cores at Sites 2 and 3 were taken to a depth of 0.90 m. At all three sites residues were found in the top 0.15 m only (Tables 7a and 7b). Concentrations at Site 1 were less than 14 μg simazine kg^{-1} soil and 57 μg diuron kg^{-1} soil. Concentrations at Sites 2 and 3 were considerably higher and quite variable. Simazine concentrations were 56.9 to 64.9 μg kg^{-1} at Site 2, and 18.5 to 104 μg kg^{-1} at Site 3. Diuron concentrations ranged from 307 to 874 μg kg^{-1} at Site 2, and 73.3 to 675 μg kg^{-1} at Site 3. Such variability should not be considered unusual, and may be attributable to the complex infiltration and transport processes that take place in soils. These have been well documented by authors such as Jury and Gruber (1989), Mulla and Annandale (1990), and van der Zee and Boesten (1991).

A final set of soil cores was taken in April 1992, after approximately 321 mm of total seasonal precipitation had been reported for the area. No pesticide residues were detected at Site 1. At Sites 2 and 3, both simazine (57 μg kg^{-1} at Site 2) and diuron (88 μg kg^{-1} at Site 2; 94 μg kg^{-1} at Site 3) were detected in the top 0.15 m only (Tables 7a and 7b).

V.2: Discharge of Runoff to Surface Water

At Site 9, 108 mm of rain were recorded at Willows between the application of simazine to the ramps of the interchange between December 9 and 11, 1991 and the first sampling event on

Table 7a. Concentrations of simazine in soil cores from rainfall simulation plots.

Date	Event	Depth[a] m	Site 1 Plot 1	Site 1 Plot 2	Site 2 Plot 1	Site 2 Plot 2	Site 2 Plot 3	Site 3 Plot 1	Site 3 Plot 2	Site 3 Plot 3
			$\mu g\ kg^{-1}$							
9/91	Background[b]	0-0.15	ND	ND	19.1	11.9	ND	ND	ND	26.3
		0.15-0.30	ND	ND	ND	ND	ND	ND	ND	694
		0.30-0.90	ND	ND	ND	ND	ND	ND	ND	ND
11/91	Post Rainfall	0-0.15	13.9	6.7	64.9	56.9	60.2	104	39.6	18.5
		0.15-0.90	ND	ND	ND	ND	ND	ND	ND	ND
		0.90-3.0	ND	ND						
4/92	Final	0-0.15	ND				57			ND
		0.15-3.0	ND				ND			ND

ND = None Detected (detection limits: 4 μg simazine kg^{-1} soil; 40 μg diuron kg^{-1} soil).

[a] Soil cores were taken in 0.15- and 0.30-m (0.5- and 1-ft) increments.

[b] Background cores were taken next to the plots.

Table 7b. Concentrations of diuron in soil cores from rainfall simulation plots.

Date	Event	Depth[a] m	Site 1 Plot 1	Site 1 Plot 2	Site 2 Plot 1	Site 2 Plot 2	Site 2 Plot 3	Site 3 Plot 1	Site 3 Plot 2	Site 3 Plot 3
			μg kg^{-1}							
9/91	Background[b]	0-0.15	ND	ND	145	122	71.5	111	58.3	143
		0.15-0.30	ND	ND	ND	80.2	ND	ND	47.3	ND
		0.30-0.90	ND	ND	ND	ND	ND	ND	ND	ND
11/91	Post Rainfall	0-0.15	56.5	ND	307	848	874	675	135	73.3
		0.15-0.90	ND	ND	ND	ND	ND	ND	ND	ND
		0.90-3.0	ND	ND						
4/92	Final	0-0.15	ND				88			94
		0.15-3.0	ND				ND			ND

ND = None Detected (detection limits: 4 μg simazine kg^{-1} soil; 40 μg diuron kg^{-1} soil).

[a] Soil cores were taken in 0.15- and 0.30-m (0.5- and 1-ft) increments.

[b] Background cores were taken next to the plots.

1 February 1992 (Table 8a). Simazine residues were detected in all runoff samples (Table 8b), with concentrations decreasing from 105 μg simazine L^{-1} runoff over a 9-hr period on February 1 to 63 μg L^{-1} over 16 hr on 14 March.

Total seasonal loss of herbicide in natural rainfall has been reported for large plots and small watersheds ranging in area from 17-m^2 plots to an 8-ha watershed (Buttle, 1990; Leonard, 1988). Seasonal losses ranged from 0.2 - 7.5 % of atrazine (the highest value was reported in a year of 2 - 3 times normal rainfall), 0.2 - 1.0 % of alachlor, 0.02 - 0.95 % of metolachlor, 0.0 - 0.5 % of trifluralin, 0.01 - 1.0 % of 2,4-D and 2,4-D salt, and 4.1 % of 2,4-D ester. In the present study, partial sampling of three rainstorms at Site 8 showed that seasonal loss from plots on the highway shoulder was greater than 8.6 % of simazine and 16.8 % of diuron (deposition calculated from application rate). Seasonal loss of simazine from the freeway interchange at Site 9, a 1.9-ha constructed watershed, was greater than 17 % (the total loss observed in partial sampling of three rainstorms). One reason for the greater losses observed in our study may be the high degree of soil compaction that can occur in the construction and use of highway roadbeds. In a study comparing runoff losses of atrazine and alachlor from wheel-compacted and noncompacted soil (in Leonard, 1988), compaction increased atrazine loss from 4.7 to 18.3 %, and alachlor loss from 8.0 to 22.1 %.

V.3: Soil Coring in Infiltration Areas

Soils at all the infiltration sites were less gravelly than soils at the simulation sites (Appendix E). Except for the top 0.15 m at Site 7, none had any particles greater than 2 mm in diameter. The SCS map units (soil types) for Sites 4-7 respectively, are Riz silty clay loam, Capay clay, Plaza silt loam (dense subsoil), and Zamora silty clay.

Two of the four sites had detectable residues in soil. No residues were detected at Site 4 or 6 at either sampling time. Standing water at Sites 4 and 6 prevented sampling in April 1992, and coring there was postponed until June. In June, ground water was encountered at 1.5 m and

Table 8a. Precipitation events pertinent to drainage sampling from one quadrant of an I-5 interchange (Site 9).

Date		Recording Location Willows[a]	
		---------------- mm (in) ----------------	
1991	12/18	12	(0.460)
	12/28-30	56	(2.22)
1992	1/5-7	27	(1.08)
	1/28	10	(0.38)
	2/1	10	(0.37)
	2/10-14	115	(4.53)
	2/18-21	41	(1.63)
	3/2	5	(0.18)
	3/5-6	31	(1.21)
	3/14	0	(0.00)
	3/16-17	57	(2.24)
	3/23	9	(0.35)
	3/30	4	(0.15)
	4/1-30	26	(1.03)
	Total	403	(15.83)

[a] Data from NOAA .

Table 8b. Herbicide concentrations in samples of storm runoff from one quadrant of an I-5 interchange (Site 9) after a simazine application to the ramps between 12/9 and 12/11/91.

Date (1992)	Sampling event	Sampling duration	Precip. [a] during sampling	Runoff [b] during sampling	Pesticide [c] in runoff sampling	
					Simazine	Diuron
		hh:mm	mm (in)	m^3	------$\mu g\ L^{-1}$------	
2/1	1	8:45	13.2 (0.52)	52-66	105	0.3
2/10	2	20:00	21.8 (0.86)	155-199	83	0.2
2/14	3	5:20	25.9 (1.02)	111-143	60	0.0
2/14	3[d]	2:00	6.9 (0.27)	>165	30	0.0
3/14	4	15:45	23.4 (0.92)	106-136	63	0.0

[a] Rainfall recorded on site.
[b] Flowsplitter collected 1.2 ± 0.15 % of total runoff (Clark and Mar, 1980). Sampling ended before runoff stopped in each event, so "runoff during sampling" is less than the total runoff for the rain event.
[c] Volume-weighted average concentration for sampling duration.
[d] After 5:20 of sampling, collection tank became submerged. Samples were taken directly from flow at 15-min intervals for two more hours.

1.8 m at Sites 4 and 6, respectively. Samples of the ground water contained no detectable herbicide residues. The additional 3.0-m infiltration cores taken at Sites 1 and 2 in April 1992 also contained no detectable residues.

At Site 5, where simazine was applied to the ramp shoulders between December 6 and 12, simazine residues were found in the 0.15-0.30 m section (26.7 $\mu g\ kg^{-1}$) and the 0.30-0.60 m section (33.0 $\mu g\ kg^{-1}$) of the core taken on 18 December (Table 9). Since the core was taken at least 6 m from any treated area, these residues were probably from the previous season's application. Simazine was detected in the upper 0.15 m at 61 $\mu g\ kg^{-1}$ on 6 April, but no residue was found below this depth. Krovar® was applied to the freeway median at this site in January 1992, but no diuron residue was found.

At Site 7, diuron was found in the upper 0.15 m at 157 $\mu g\ kg^{-1}$ on 19 December (Table 9). Simazine and diuron were applied to the shoulder between January 13 and 16. On 6 April, simazine was found in the 0.30-0.60 m section at 29 $\mu g\ kg^{-1}$, and diuron was found at an average concentration of 136 $\mu g\ kg^{-1}$ to a depth of 0.30 m.

V.4: Impact of Regional Highway Runoff on Surface Waters

A very rough estimate was made of simazine and diuron concentrations in highway runoff from eastern Glenn County after a large storm, using data from Sites 8 and 9 for the sampled portions of the storm of February 9 and 10, 1992. The estimate applies only to runoff coming from highway ROW. It does not consider herbicide runoff from airports, irrigation canals, levees, railroad ROW or agricultural areas. (Note that ROW uses accounted for only 22 % of all simazine and 46 % of all diuron used in Glenn County in 1990, the rest being used in agricultural crops such as walnuts, almonds, grapes, and olives (CDFA, 1990).) Neither is dilution by runoff from untreated areas considered. The data to estimate these contributions were not available.

Table 9. Concentrations of simazine and diuron in soil cores[a] from infiltration Sites 5 and 7[b].

Date	Depth[e] m	Site 5[c] Simazine (µg kg⁻¹)	Site 5[c] Diuron (µg kg⁻¹)	Depth m	Site 7[d] Simazine (µg kg⁻¹)	Site 7[d] Diuron (µg kg⁻¹)
18-19 December 1991	0-0.15	ND	ND	0-0.15	ND	157
	0.15-0.30	26.7	ND	0.15-0.30	ND	ND
	0.30-0.60	33.0	ND	0.30-0.60	ND	ND
	0.60-3.0	ND	ND	0.60-3.0	ND	ND
6 April 1992	0-0.15	61	ND	0-0.15	140	140
	0.15-0.30	ND	ND	0.15-0.30	137	132
	0.30-0.60	ND	ND	0.30-0.60	29	ND
	0.60-3.0	ND	ND	0.60-3.0	ND	ND

ND = None Detected (detection limits: 4 μg simazine kg^{-1} soil; 40 μg diuron kg^{-1} soil).
[a] One 3.0 m (10ft) core was taken on each date at each site.
[b] Samples taken at Sites 4 and 6 contained no detectable simazine or diuron.
[c] Princep applications made on 12/6/91-12/11/91; Krovar applied 1/13/92.
[d] Princep and Karmex applications made on 1/13/92.
[e] Soil cores were taken on 0.5- and 1-ft increments (0.15- 0.30-m).

In Fall 1991 and Winter 1992, Caltrans applied simazine, diuron or both to both sides of approximately 97 km of road, and to portions of 48 km of I-5 in Glenn County (Table 10 and Fig. 7). The county applied simazine or diuron to both sides of 1290 km of road (Table 10 and Fig. 8). Caltrans also applied simazine to nine I-5 interchanges with 25 quadrants that drain to outside surface channels.

Site 8, on Highway 45, was used to represent all of the state and county roads treated by Caltrans and Glenn County. Site 9, where effluent was collected from an I-5 interchange, was used to represent all 25 interchange quadrants. Measured runoff volume at Site 8 during the sampling of 9 February, extrapolated to 72 m^3 runoff km^{-1} of highway, was multiplied by the total number of treated km. (For this calculation, I-5 kilometers were doubled, since the freeway actually comprises two 2-lane roads.) Runoff volume at Site 9 during the sampling of 10 February, approximately 177 m^3, was multiplied by 25 quadrants. Total highway runoff volume thus estimated was approximately 218,000 m^3. Herbicide mass loss was calculated using mass km^{-1} at Site 8 (Table 6) multiplied by the total number of km treated. For this calculation, I-5 kilometers were not included because few are treated with both chemicals and many are treated with neither. Roads were treated by the County at different application rates, so mass loss from County kilometers was weighted by the ratio of the actual rate to the rate at Site 8. Mass loss from Site 9 of 14.7 g simazine was multiplied by 25 quadrants. Total mass loss was thus calculated to be 33.4 kg simazine and 58.3 kg diuron. If this runoff were completely mixed, it would have herbicide concentrations of 153 μg simazine and 267 μg diuron L^{-1}.

The hypothetical simazine and diuron concentrations in the mixed runoff are below all but one of the short-term toxicity levels reported in Table 11. The 96-hr LC_{50} of diuron for the freshwater invertebrate would be exceeded, so it would be important to determine whether these concentrations would last longer than the 20 - 28 hr observation period. Similarly, although these concentrations exceed lifetime safe levels for humans, they would be expected to occur only during rainstorms. However, undiluted runoff from the shoulder at Site 8 contained diuron

Table 10. ROW uses of simazine and diuron in Glenn County from Fall 1991 until Spring 1992[a].

User	Extent of Responsibility	Active Ingredient	Percent of Total ROW Use of	
			Simazine[a]	Diuron[b]
CalTrans	97 km (60 mi) roads[d] 48 km (30 mi) of I-5	simazine and/or diuron	27	14
Glenn County	1290 km (800 mi) roads[e] 80 km (50 mi) river levee	simazine or diuron	72	37
Southern Pacific Railraod	105 km (65 mi) track	diuron	0	26
Glenn-Colusa Irrig. District	65 km (40 mi) canal	diuron	0	21
Others			1	2

[a] Source: Monthly summaries of use reports submitted to Glenn Co. Ag. Comm.
[b] Total ROW use 752 kg (1650 lbs).
[c] Total ROW use 1480 kg (3260 lbs).
[d] Extent of responsibility includes shoulders on both sides of the road.
[e] Extent of responsibility includes shoulders on both sides of the road, medians, and interchange ramps.

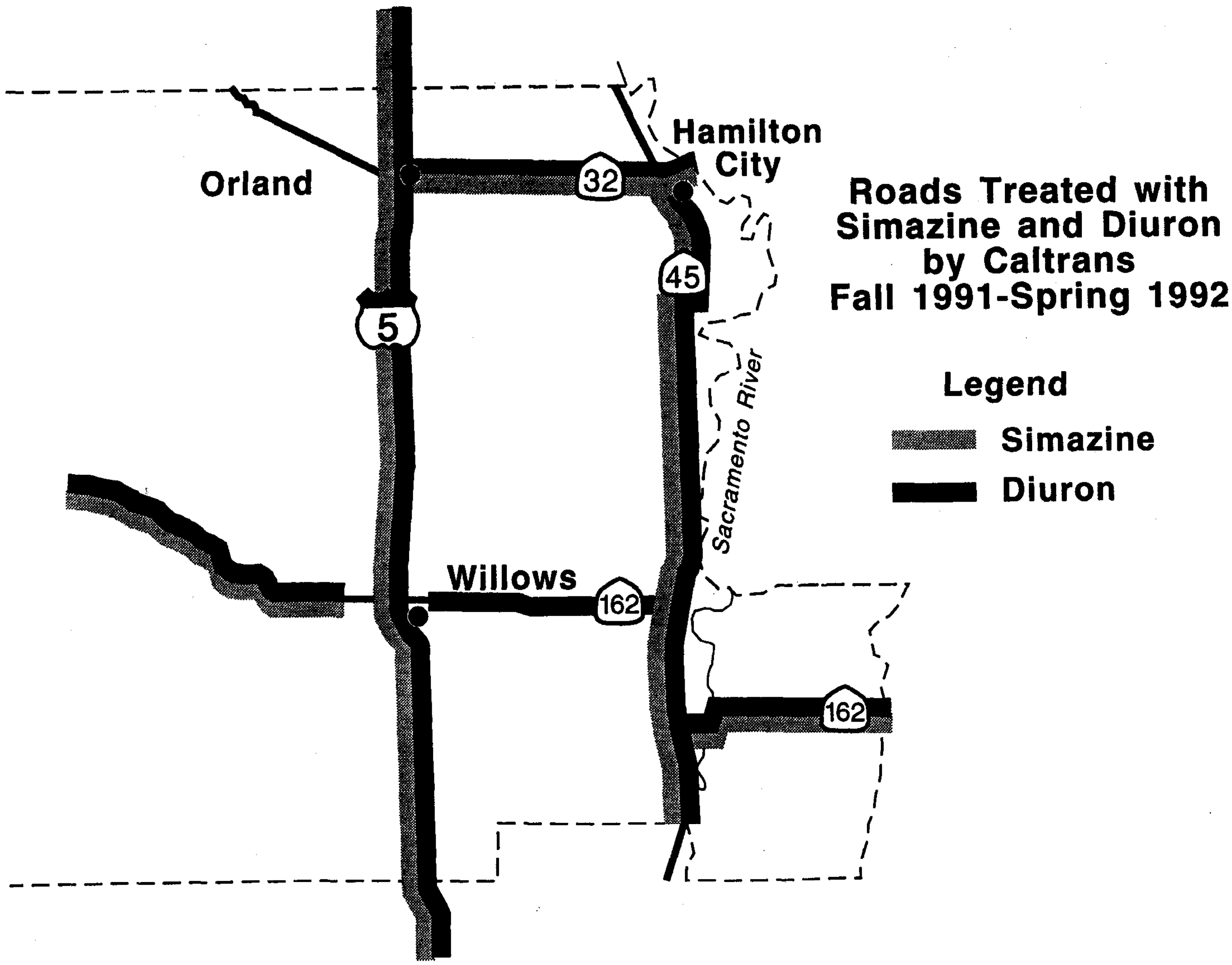

Fig. 7. Roads treated with simazine and diuron by Caltrans, Fall 1991- Spring 1992. Coverage of I-5 was interrupted by numerous untreated segments.

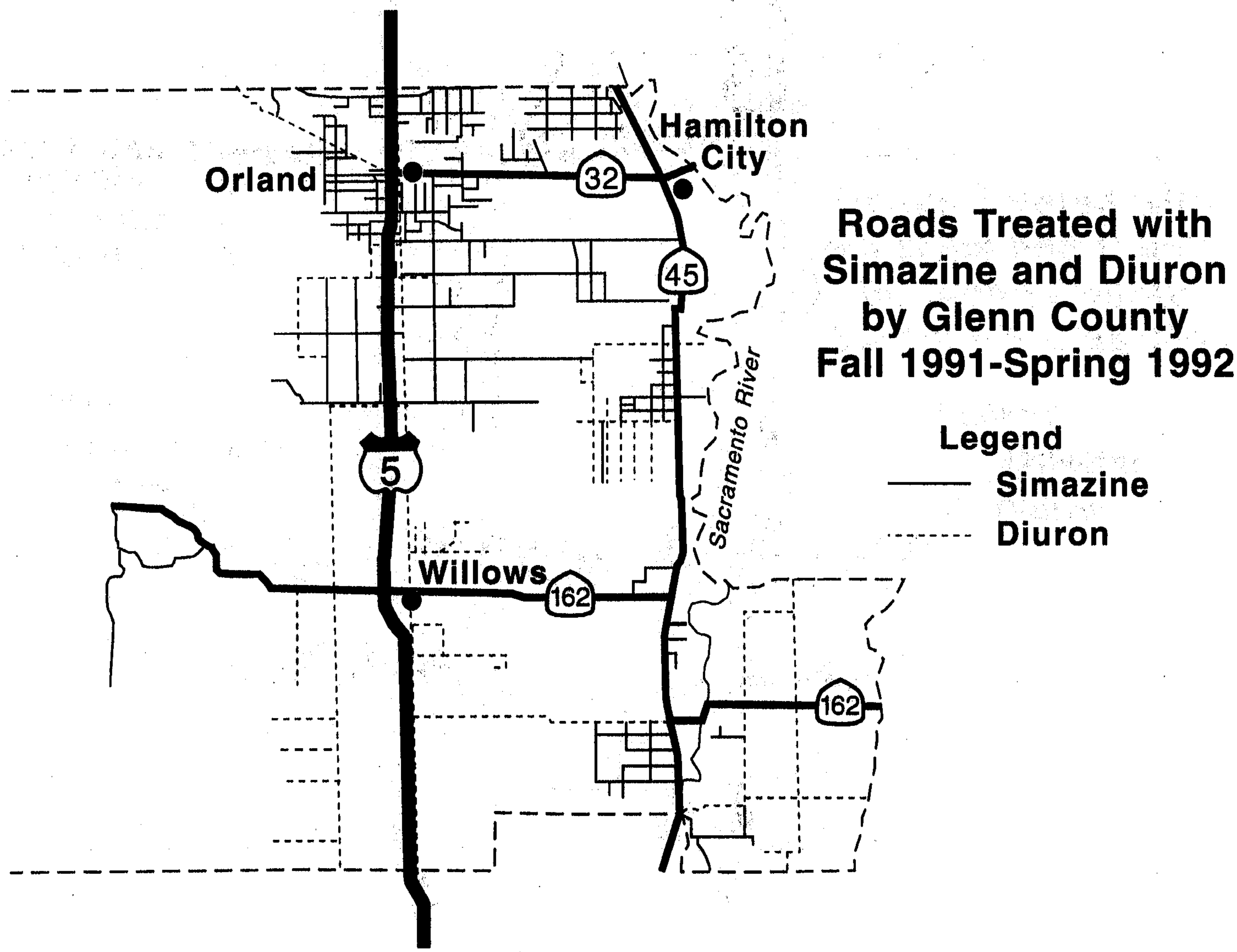

Fig. 8. Roads treated with simazine or diuron by Glenn County Agricultural Commissioner, Fall 1991-Spring 1992.

Table 11. Toxicity of simazine and diuron.

	Simazine $\mu g\ L^{-1}$	Diuron $\mu g\ L^{-1}$
Human		
EPA Lifetime HAL[a] (adult)	4[b]	10
EPA 10-day HAL[a] (child)	70	1000
Theoretical Cancer Risk of 10^{-6} (adult)	0.3[c]	-
Freshwater Fish[d]		
24-hr LC50	7600[e]	2800[f]
96-hr LC50	5000[e]	710[f]
Freshwater Invertebrate[d]		
24-hr LC50	>5600[g]	700[h]
96-hr LC50	1900[g]	160[h]

[a] Health Advisory Levels (not enforceable standard): USEPA Safe Drinking Water Hotline (1-800-426-4791), Jan. 14, 1993.
[b] Lifetime HAL value for simazine is also a Maximum Contaminant Level (an enforceable standard).
[c] Federal Reg. Vol.5, No.38. Friday July 17, 1992, p 31793-31795.
[d] Most sensitive species reported in Mayer and Ellersieck (1986).
[e] Fathead Minnow.
[f] Cutthroat Trout.
[g] Pteronarcys californicus.
[h] Gammarus fasciatus.

concentrations high enough (1027 $\mu g\ L^{-1}$) to be lethal to freshwater invertebrates, should they be present in the drainage ditches immediately adjacent to ROW.

V.5: Suggestions for Further Research

The findings of this study suggest three areas for further research.

1. The possibility that pesticides may be transported rapidly through highway shoulders of gravelly composition suggests a more thorough investigation of preferential flow through this type of material. This could be one type of direct conduit to ground water.

2. Substantial amounts of diuron were applied by Southern Pacific Railroad and the Glenn-Colusa Irrigation District, in places at rates over three times those used by Caltrans (Table 10). The fate of this runoff needs to be investigated since it could have concentrations of diuron lethal to aquatic life.

3. Herbicide concentrations were high in the sediment carried in runoff. Accumulation of contaminated sediment in wildlife refuges and other wetlands may pose a problem, especially as both simazine and diuron are quite persistent in soil (diuron aerobic half-life 372 days; diuron anaerobic half-life 995 days; simazine aerobic half-life 110 - 258 days; simazine anaerobic half-life 58 - 84 days (DPR Pesticide Chemistry Database, 1995)). An evaluation of sediment load under standardized runoff conditions, and sediment monitoring data from an area such as the Sacramento Wildlife Refuge, would be valuable.

VI. SUMMARY AND CONCLUSIONS

VI.1: Runoff Experiment

Simazine and diuron were detected at two of three sites in the runoff of one hr of simulated rainfall from highway shoulder plots. Concentrations were as high as 574 μg simazine L^{-1}runoff and 1770 μg diuron L^{-1} runoff (combined water and sediment), observed one day after herbicide application. From 0.2 - 2.3 % of the simazine and 0.2 - 5.4 % of the diuron applied to highway shoulders was removed in runoff during one simulation. The highest percentages were observed when rain was simulated 1 day after herbicide application. Post-simulation and end-of-season soil cores had detectable simazine and diuron residues only in the top 0.15 m (0.5 ft). However, cores taken prior to application had both simazine and diuron down to 0.30 m, ostensibly from the previous year's application.

At the other simulation site, no runoff left the plots. The absence of detectable residues in soil to a depth of 3.0 m (10 ft) suggests that much of the herbicide applied to the shoulder may have leached rapidly through the coarse gravelly soil.

Herbicides concentrations in actual storm runoff from highway shoulders were between 29 and 377 μg simazine L^{-1} runoff and between 46 and 2849 μg diuron L^{-1} runoff. The highest concentrations were observed in the first sampled storm, after up to 25 mm of rain had already fallen since the herbicide application. Higher concentrations would be expected in runoff from rainfall events closer to the time of application. More than 8.6 % of the simazine and more than 16.8 % of the diuron applied were removed from the shoulder plots during the combined sampling periods; these percentages represent less than total seasonal loss because sampling of rainstorms was not complete.

VI.2: Discharge of Runoff to Surface Water

Simazine was detected in all samples of runoff discharged into surface water from a freeway interchange treated with simazine. The maximum average event concentration of 105 $\mu g\ L^{-1}$ over a 9-hr period was seen in the earliest of three sampled rain storms (7 wk after simazine application). Concentrations dropped as the rainy season progressed. Thirteen weeks after application, simazine concentration averaged 63 $\mu g\ L^{-1}$ over a 16-hr period.

Combined mass loss during all sampling was 17.4 % of the estimated target application. The four sampled rainfall events accounted for only 24% of the season's precipitation, suggesting that a considerably larger amount of simazine may have been discharged in total.

Based on the limited information collected during this study, the levels of simazine and diuron in ROW runoff would probably not constitute a health problem for humans, especially since drinking water is not derived from these sources. However, undiluted runoff could contain levels of diuron that would be lethal to freshwater invertebrates. This may be of special concern where treated ROW, including railroads and canal levees, are in close proximity to wetlands or wildlife refuges.

VI.3: Leaching in Infiltration Areas

No evidence was found of deep infiltration of simazine or diuron through soil. Simazine and diuron were detected in soil at two of four runoff infiltration sites, to a maximum depth of 0.60 m. At one site, no downward movement was seen over the four months following application. At the other site, no conclusions were drawn about movement because the herbicide application occurred after the first sample was collected.

The quantity of soil data collected was insufficient to yield definite conclusions about leaching in infiltration areas. However, even if leaching is relatively minor in these areas, the levels of simazine and diuron we found in runoff suggest that dry wells, if present, might provide a very important conduit for the transport of these herbicides to ground water. It should also be noted that ROW areas with high percentages of gravel and sand in the soil may be of concern, since herbicides may be transported rapidly to depths greater than 0.30 m.

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APPENDIX A

English-Metric Conversion Factors

Appendix A Table 1: **English-Metric Conversion Factors**

	UNITS	
	English	Metric
Rainfall	1 inch	26 mm
Pesticide application rates	1.8 lb. $acre^{-1}$	2.02 kg simazine ai ha^{-1}
	3.2 lb. $acre^{-1}$	3.59 kg diuron ai ha^{-1}
	3.6 lb. $acre^{-1}$	4.03 kg simazine ai ha^{-1}
	2.0 lb. $acre^{-1}$	2.24 kg diuron ai ha^{-1}
Swath widths	4-ft	1.2-m
Distance	1 mile	1.6 km
Soil cores	1 foot	0.30 m
Area	1 ft^2	0.093 m^2
Volume	1 gal 1 cf	3.8 L 0.028 m^3

APPENDIX B

Chemical Methods for the Determination of Simazine and Diuron
on Various Media.

CALIFORNIA DEPT. OF FOOD & AGRICULTURE.
CHEMISTRY LABORATORY SERVICES
ENVIRONMENTAL MONITORING SECTION
3292 Meadowview Road
Sacramento, CA 95832
(916) 262-2080
Fax (916) 262-2082

Original Date: September 10, 1991
Supercedes: NEW
Current Date: March 25, 1993
Method #:

DIURON AND SIMAZINE ON KIMBIES

SCOPE:

This method has been used to determine Simazine and Diuron on roadside Kimbies.

PRINCIPLE:

Simazine and Diuron are extracted from kimbies by shaking them with methanol. The extract is concentrated and filtered through a micro Acrodisc before analysis by both gas and liquid chromatography.

REAGENTS AND EQUIPMENT:

Methanol, pesticide grade and suitable for HPLC
Glass jar, (1000 mL)
Mechanical shaker (G 10 Gyrotory Shaker) New Brunswich Scientific
Graduated cylinder, (1000 mL)
Boiling flask, (500 mL)
Graduated test tube, (15 mL)
Micro Acrodisc, 0.2 µm
Nitrogen evaporator - Meyer N-EVAP (Model 112) Organomation Associates, Inc.

ANALYSIS:

1) Place a kimbie in a 1000 mL jar. Add 500 mL of methanol to the jar. Shake the jar for 1 hour at 200 rpm by using the G 10 mechanical shaker.

2) The sample is injected directly on GC and LC after filtering through a micro filter.

3) If the sample has high concentrations of Simazine or Diuron, the sample should be diluted to fall into the linear dynamic range which is from 0.1 ng to 20 ng.

4) If the pesticides are not detected in the step # 2 above, quantitatively take a 150 mL aliquot from the jar and place into a 500 mL round bottom flask. Evaporate on the rotory evaporator at 55 °C to just dryness and wash the sides of the flask with about 12 mL of methanol and transfer the residue to a graduated test tube.

ANALYSIS: continued

5) Concentrate to 3 mL on the N-EVAP set at 40 °C. Filter the extract and inject on the GC and LC.

EQUIPMENT CONDITIONS:

A. GAS CHROMATOGRAPHY : HP 3700 with TSD

Column: HP - FFAP (10m x 0.53 mm. Film thickness: 1.0μm)

Temperature program: Initial: 150 °C.
Hold: 1 minute
Rate: 10 °C/minute
Final: 220 °C.
Hold: 2 minutes

Injector: 220 °C

Detector: 220 °C.

Carrier gas: Helium, flow rate: 20.0 mL/minute

Sample inject: 2 μL.

Retention time for **Simazine** ~ 8.30 minutes

B. LIQUID CHROMATOGRAPHY: Perkin Elmer Series 4 with a UV detector.

Column: Beckman ODS, 5.0 μm, 4.6 mm x 15.0 cm.

Guard column: Beckman ODS, 5.0 μm x 4.6 mm x 4.5 cm.

Detector: Varian 2550 UV.

Flow rate: 1.0 mL/min.

Sample inject: 40 μL.

Mobile phase: 45% acetonitrile, 55% water.

Wave length: 254 nm.

Retention time for **Diuron** ~ 5.6 minutes

EQUIPMENT CONDITIONS: continued

C. CONFIRMATION: Simazine and Diuron were confirmed on Tremetrics Photo-Conductivity Detector model 925 with the following conditions:

Mobile phase: 45% acetonitrile, 55% water.

Column: Beckman ODS, (5.0 µm x 4.6 mm x 25 cm)

UV source: Mercury lamp.

Flow rate: 1.0 mL/minute

Chart speed: 0.5 inch/minute

Range: 10, attenuation 1

Sample inject: 25 µL

Retention time: Simazine ~8 minute, Diuron ~15.0 minute

Both Simazine and Diuron are confirmed at MDL (S/N = 20/1) which is 0.5 ug per sample (kimbics)

RESULTS:

CALCULATION:

$$\text{Microgram per sample} = \frac{\text{(peak height sample) x (ng std) x (final volume in mL)}}{\text{(peak height std) x (uL sample injected)}}$$

DISCUSSION :

The following results were calculated from three different spike levels. These spikes were as follows: Level 1 - Diuron - 18.08 mg with 9.0 mg Simazine, Level 2 - Diuron - 36.16 mg with 18.0 mg Simazine, and Level 3 - Diuron 54.24 mg with 27.0 mg of Simazine.

DISCUSSION : continued

CHEMICAL	SPIKE LEVEL (mg)	(%) RECOVERY	$\bar{x}$	SD	% CV	n
Diuron	18.08	92.70	16.76	2.50	2.69	5
	36.16	95.46	34.52	1.87	1.96	5
	54.24	90.18	48.91	5.06	5.61	5
Simazine	9.0	101.22	9.11	3.88	3.83	5
	18.0	93.24	16.78	2.07	2.22	5
	27.0	93.40	25.22	8.94	9.57	5

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Original Date:03/24/1990
Supercedes: NEW
Current Date:04/10/1990
Method #:

MULTIPESTICIDE RESIDUE ANALYSIS: ATRAZINE, BROMACIL, DIURON, PROMETON, SIMAZINE IN WELL WATER.

SCOPE:

This method is developed to analyze Atrazine, Bromacil, Diuron, Prometon, and Simazine in well water.

PRINCIPLE:

A conditioned C 18 reversed phase Sep-pak is used to trap Atrazine, Bromacil, Diuron, Prometon and Simazine from water samples. The Sep-pack is then centrifuged to eliminated any remaining water. Methanol is then used to elute all chemicals. The eluant is then concentrated and analyzed for Diuron and Bromacil by LC, for Atrazine, Prometon, Simazine by GC.

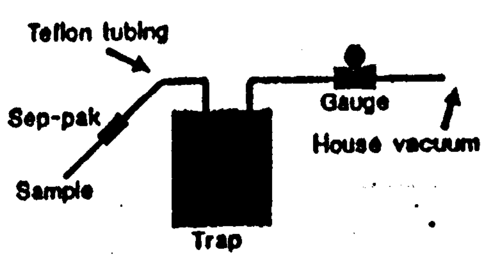
REAGENTS AND EQUIPMENT:

Methanol, pesticide grade or equivalent.
Distilled water.
Working standards in Methanol (Diluted from stock standard.)
In house vacuum manifold.
In house aspiration system.
C18 reversed phase Sep-pak,® Water Division of Millipore.
Nylon acrodisc, 0.2 micron, Gelman Sciences.
Centrifuge: Clay Adams.
Beakers, 600 mL.
Graduated test tubes, 10 mL.
Micro-Mate Syringes, 10 cc - Popper & Sons Inc.
N-EVAP - Meyers Organomation Associates Incorporated
Vibrating mixer.
Sodium Sulfate, anhydrous, granular (ACS).

ANALYSIS:

1. For each sample, weigh 500.0 grams of water sample into two separated 600ml beakers.
2. Connect a C 18 reversed phase Sep-pak to the in house vacuum manifold as follows in diagram #1.

Diagram #1



ANALYSIS:

3. Condition the Sep-pak with about 5 mL of methanol followed by about 10 mL of distilled water by applying in house vacuum. <u>Do not let the sep-pak go to dryness.</u>
4. Attach the conditioned Sep pak to a 15 mm glass tubing and dip into the beaker containing the 500g of sample. Adjust the flow rate to about 3-5 ml/minute (about 6 in Hg).
5. After all 500g of water sample has passed through the Sep-pak, leave the vacuum on for few minutes.
6. Remove the Sep-pak and insert the sep-pak into a centrifuge tube and centrifuge for 1 minute at 1200 rpm by setting the dial at 4 on the centrifuge.
7. Elute all chemicals with 8 mL of methanol by using the in house aspiration system into a 10 mL graduate test tube.
8. Concentrate the eluting solvent to 1.0 mL by using the Nitrogen evaporator. Mix it well for 30 seconds by using the vibrating mixer. Filter through a 0.2 um acrodisc into three separated micro vials.

Analyze by gas chromatograph and liquid chromatograph

EQUIPMENT CONDITIONS:

A. Gas chromatograph: HP 3700 with TSD.
   Column: HP-17 10 m x 0.53 mm. Film thickness: 2.0 um.
   Temperature program: Isothermal 175°C.
   Injector: 220°C, detector: 220°C.
   Carrier gas: Helium. Flow rate: 20 mL/min.
   Sample injected: 2 ul.
   Retention times: Prometon ~ 2.40 minutes
   Atrazine ~ 2.82 minutes
   Simazine ~ 3.04 minutes

B. Liquid chromatography: Perkin Elmer Series 4.
   Column: BECKMAN ODS, 5.0 um, 4.6 mm x 15.0 cm.
   Guard column: BECKMAN ODS, 5.0 um, 4.6 mm x 4.5 cm.
   Detector: Varian 2550 UV.
   Flow rate: 1.0 ml/min.
   Sample injected: 60 ul.

   For Diuron analysis:
   Mobile phase: 55% water, 45% acetonitrile.
   Wave length: 254 nm.
   Retention time: ~ 5.60 minutes.

   For Bromacil analysis:
   Movile phase: 70% water, 30% acetonitrile.
   Wave length: 280 nm.
   Retention time: ~ 5.14 minutes.

CONFIRMATION: Atrazine, Promoton and Simazine are confirmed by Varian 6000 with TSD. Column: 20 m x 0.53 mm x 1.3 um Carbowax.
Injector: 220°C, detector: 220°C.
Temperature program: Int:150°C.
Int time: 0 min.
Rate: 15°C/min.
Final time: 9 min.
Carrier gas: Helium. Flow rate:25 mL/min.

Retention times: Prometon ~ 5.7 minutes.
Atrazine ~ 7.8 minutes.
Simazine ~ 9.3 minutes.

Bromacil is confirmed by TSD/DB-1301 30 m x 0.53 mm x 1.0 um column.
Carrier gas: Helium. Flow rate: 25 mL/min.
Isothermal 190°C, injector: 220°C, detector: 220°C.
Retention time:~ 8.9 minutes.
Diuron *is not confirmed at MDL level.*

CALCULATIONS:

$$PPB = \frac{\text{Peak height of sample} \times \text{Amount of std(ng)} \times 1{,}000\text{ul}}{\text{Peak height of std} \times \text{volume injected} \times \text{sample weight(g)}}$$

DISCUSSION:

Minimum detection limit (Signal to noise ratio is 5 to 1.) for these chemicals by this method was 0.1ppb.

DIODE ARRAY DETECTOR was tried to analyze bromacil and diuron. However, the sensitivity did not meet the requirement.

The diagram #1 is a in house system. If you have any question about it, please contact the above address.

The following results were obtained from different spike levels by multipoints calibration method:

Chemical	Spike level (ppb)	Number of analysis (n)	Mean % Recovery	Standard deviation (+/-)
Atrazine	4.0	5	102.7	7.9
Prometon	4.0	5	105.5	9.6
Simazine	4.0	5	107.4	8.8
Bromacil	4.0	5	103.5	6.2
Diuron	4.0	5	102.2	4.7

DISCUSSION:

Chemical	Spike level (ppb)	Number of analysis (n)	Mean % Recovery	Standard Deviation (+/-)
Atrazine	2.0	5	90.4	3.5
Prometon	2.0	5	91.5	4.8
Simazine	2.0	5	89.4	6.6
Bromacil	2.0	5	87.7	6.8
Diuron	2.0	5	88.2	7.2
Atrazine	0.5	10	106.8	13.3
Prometon	0.5	10	103.0	6.9
Simazine	0.5	10	105.6	15.6
Bromacil	0.5	10	92.0	9.7
Diuron	0.5	10	99.6	14.8

REFERENCES:

WRITTEN BY: Duc Tran

DTran

TITLE: Agricultural Chemist I

REVIEWED BY: Catherine Cooper

Catherine Cooper

TITLE: Agricultural Chemist III

APPROVED BY: S. Mark Lee

S. Mark Lee

TITLE: Principal Investigator

To: Nancy Miller
Assoc. Environment Research Scientist
Environment Hazards Assessment Program

Date: 8/22/1991
Place: Sacramento

From: Duc Tran
Ag. Chemist
Chemistry Lab Services

Subject: Silicone, Mineral Spirits, and Plaster adhesive interference testing for Simazine and Diuron in water.

We conducted the following experiment in order to see whether or not a mixture of provided Silicone and Mineral spirits or Plaster adhesive alone have any effects on the recoveries of Simazine and Diuron from water by using our method (Solid Phase Extraction).

We weighed 14.0g of a 50:50 (w/w) mixture Silicone and Mineral spirits. The mixture was spread evenly on 28 x 21 cm printer paper and allowed to dry overnight. The paper was divided into 3 equal parts. Each part was cut into small strips and transfered to a flask containing a 0.4 ppb water spike. The spike was then extracted by our method for analyzing Atrazine, Prometon, Simazine, Bromacil and Diuron in water. For the Plaster adhesive, we followed the same procedure. The contact time between the above materials and spiking solution was approximately 30 minutes total.

The results are tabulated below:

Chemical	Blank (plus the blank paper)	0.4 ppb	0.4 ppb (plus the mixture)	0.4 ppb (plus the adhesive)
Diuron	ND	..37 ppb	.37 ppb	.32 ppb
	ND	.37 ppb	.40 ppb	.37 ppb
		.40 ppb	.35 ppb	.32 ppb
		.36 ppb		
Simazine	ND	.39 ppb	.35 ppb	.34 ppb
	ND	.38 ppb	.37 ppb	.35 ppb
		.35 ppb	.38 ppb	.37 ppb
		.35 ppb		

The results indicate that there are no major interferences from the materials tested on the recoveries of Simazine and Diuron from a water sample using our Solid Phase Extraction method.

cc: Catherine Cooper
Sally Powell

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Original Date: 07/20/90
Supercedes:
Current Date:09/04/90
Method #:

RESIDUE ANALYSIS OF TRIAZINES IN SOIL

SCOPE:

This method was developed for the chemical analysis of Bromacil, Diuron, Prometone, Atrazine, and Simazine in soil.

PRINCIPLE:

The chemicals aré extracted from soil with a mixture of hexane:acetone. An aliquot is concentrated to eliminate acetone (Azeotrope:49.8°C) and then transfered to a pre-conditioned silica gel Sep-pak®. After the Sep-pak® is washed with hexane, all chemicals are eluted with methanol.

REAGENTS AND EQUIPMENT:

Acetone, pesticide grade
Hexane, pesticide grade
Methanol, pesticide grade
Sodium Sulfate, anhydrous, granular (ACS)
Bottles, 500 mL amber wide-mouth with lid
Graduate cylinder, 100 mL
Funnels, 60° short stem, 3-4 inch diameter
Graduate test tube, 15 mL
Whatman #1 filter paper, 12.5 cm
Micro-Mate® Syringes, 10 cc - Popper & Sons Inc.
Nylon Acrodisc®, 0.2 micron, Gelman Sciences
Sep-pak® silica gel, Waters and Associates
Balance - Mettler PL 1200, Mettler Instrument Corp.
G-10 Gyrotory® Shaker with CE-250S clamps, New Brunswick Scientific Co., Inc.
Evaporator with nitrogen blow-down,(Model #12), Organomation Associates Inc.
Vortex mixer
Centrifuge, Clay Adams (Model #0005)
Pipette

ANALYSIS:

1) Weigh 25 g of soil into a 500 mL brown bottle. Add 30 g of sodium sulfate and 50 mL of a hexane:acetone (60:40) mixture.

2) The sample bottle was shaken for two hours at 210 rpm on a mechanical shaker.

3) Decant the extract through a funnel containing filter paper and 20 g sodium sulfate into a 100 mL graduated cylinder.

4) Add 20 mL of the hexane:acetone (60:40) mixture to the brown bottle and shake it for 1-2 minutes. Decant the extract into the cylinder. Wash the funnel with about 10 mL of hexane:acetone (40:60) and bring the volume to 75 mL with the mixture.

5) Pipet 15 mL of the extract into a graduated test tube. Concentrate to 1.0 mL using a nitrogen evaporator set at 45°C. Add 1 mL of hexane to the test tube and 2 g of anhydrous sodium sulfate. Mix well on a vortex mixer.

6) Connect a silica gel Sep-pak® to a 10 mL syringe. Condition the Sep-pak® by adding 4 mL of hexane and slowly pressing the plunger to obtain a flow rate about 3 mL/min. Maintain this flowrate if possible

7) Quantitatively transfer the extract from the test tube to the syringe with the conditioned silica gel Sep-pak®. Pass the extract through the Sep-pak® discarding the solvent.

8) Wash the Sep-pak® with 4 mL of hexane. Discard the expelled solvent. Centrifuge the Sep-pak® at 1100 rpm about for 30 seconds.

9) Reconnect the Sep-pak® to the syringe and add 10 mL of methanol to the syringe and elute. Collect the sample extract in a graduated test tube.

10) Concentrate the eluant to 3 mL, using the evaporator with nitrogen. Filter through an Acrodisc® into 2 autosampler vials. Analyze Prometone, Atrazine and Simazine by GC/NPD. Bromacil and Diuron are analyzed by HPLC/UV.

EQUIPMENT CONDITIONS:

PRIMARY ANALYSIS:

Gas chromatograph: Varian 6000 with TSD
Column: HP-Carbowax 20M (polyethylene glycol) 30 m x 0.53 mm x 1.33 um
Carrier gas: Helium: Flow rate: 20 mL/min
Injector: 210°C
Detector: 250°C
Temperature program: Initial temp: 130°C
Rate: 15°C/min
Level 1 temp: 190°C
Hold time: 0 min
Final temp: 220°C
Rate: 25°C/min
Hold time: 1 min
Sample injected: 2 uL
Retention times: Prometone = 3.2 min
Atrazine = 4.1 min
Simazine = 4.5 min

Linearity checked: 0.2 ng - 20 ng

Liquid chromatograph: Perkin Elmer Series 4
Column: Beckman ODS, 5.0 um, 4.6 mm x 25.0 cm
Guard column: Beckman ODS, 5.0 um, 4.6 mm x 4.5 cm
Detector: Varian 2550 UV
Flow rate:1 ml/min
Sample injected: 40 ul

For Diuron analysis:
Mobile phase: 55% Water, 45% Acetonitrile
Wavelength: 254 nm
Retention time: Diuron - 5.6 min
Linearity checked: 0.2 ng - 100 ng

For Bromacil analysis:
Mobile phase: 70% Water, 30% Acetonitrile
Wavelength: 280 nm
Retention time: Bromacil - 5.14 min
Linearity checked: 0.2 ng - 100 ng

CONFIRMATION ANALYSIS:

Gas Chromatograph: Varian 3700 GC with FPD
Column: HP-17 (50% phenyl, 50% methyl-polysiloxane) 10 m x 0.53 mm x 2.0 um
Carrier gas: Helium, flow rate: 15 mL/min
Injector: 200°C
Detector: 250°C
Temperature program: Initial temp: 175°C held for 5 min
Rate: 35°C/min
Final temp: 220°C held for 4 min
Injection volume: 2 uL
Retention times: Prometone - 4.4 min
Atrazine - 4.7 min
Simazine - 4.9 min
Linearity checked: 0.2 ng - 20 ng

For Diuron confirmation:
Varian 6000 with TSD
Column: HP-1 (100% dimethyl polysiloxane) 10 m x 0.53 mm x 1.33 um
Carrier gas: Helium: Flow rate: 20 mL/min
Injector: 210°C
Detector: 250°C
Temperature program: Initial temp: 170°C held for 1 min
Rate: 10°C/min
Final temp: 220°C held for 1 min
Sample injected: 2 ul
Retention time: Diuron - 3.2 min
Linearity checked: 0.2 ng - 20 ng

CONFIRMATION ANALYSIS:

For Bromacil confirmation:
Varian 6000 GC WITH TSD
Column: DB-1301 (6% cyanopropylphenyl & 94% methyl) 30 m x 0.55 mm x 1.0 um
Carrier gas: Helium, flow rate: 20 mL/min
Injector: 220°C
Detector: 300°C
Temperature: 190°C isothermal
Injection volume: 2 uL
Retention time: Bromacil = 4.2 min
Linearity checked: 0.2 ng - 20 ng

The following results were obtained by the above method:

Sandy Soil

Chemical	Spike level (ppm)	Number of analyses (n)	Mean % Recovery	Standard Deviation* (±)
Atrazine	0.5	5	87.2	9.86
Prometone	0.5	5	86.0	10.00
Simazine	0.5	5	86.8	8.79
Bromacil	0.5	5	94.8	9.01
Diuron	0.5	5	83.2	6.42
Atrazine	2.0	5	78.6	5.76
Prometone	2.0	5	76.4	5.76
Simazine	2.0	5	78.9	5.72
Bromacil	2.0	5	85.5	3.23
Diuron	2.0	5	73.4	3.40
Atrazine	10.0	5	75.0	6.57
Prometone	10.0	5	89.2	6.56
Simazine	10.0	5	71.9	6.97
Bromacil	10.0	5	83.2	4.97
Diuron	10.0	5	87.8	4.37
Atrazine	40.0	5	75.8	6.74
Prometone	40.0	5	77.8	5.16
Simazine	40.0	5	66.4	6.26
Bromacil	40.0	5	80.6	4.34
Diuron	40.0	5	90.4	3.41

*Standard deviation of the spike recoveries.

Clay Soil

Chemical	Spike level (ppm)	Number of analyses (n)	Mean % Recovery	Standard Deviation (±)
Atrazine	0.5	5	68.4	2.97
Prometone	0.5	5	79.2	3.35
Simazine	0.5	5	68.0	3.16
Bromacil	0.5	5	72.4	3.58
Diuron	0.5	5	87.6	9.32
Atrazine	2.0	5	69.7	2.46
Prometone	2.0	5	73.5	3.00
Simazine	2.0	5	69.0	1.41
Bromacil	2.0	5	80.3	3.37
Diuron	2.0	5	92.4	5.02
Atrazine	10.0	5	90.6	2.67
Prometone	10.0	5	97.8	2.81
Simazine	10.0	5	85.7	4.03
Bromacil	10.0	5	80.3	2.45
Diuron	10.0	5	89.7	7.00
Atrazine	40.0	5	88.8	12.23
Prometone	40.0	5	87.4	8.60
Simazine	40.0	5	85.7	12.97
Bromacil	40.0	5	75.5	3.65
Diuron	40.0	5	89.8	4.24

CALCULATIONS:

$$\text{ppm} = \frac{(\text{peak height sample})(\text{ng/uL std})(\text{uL injected std})(\text{final volume (3 mL)})}{(\text{peak height std})(\text{uL injected sample})(\text{sample weight (5g)})}$$

DISCUSSION:

The minimum detection limit (MDL) for Bromacil by this method was 0.1 ppm and 0.05 ppm for Diuron, Atrazine, Simazine and Prometone. We can lower the MDL by increasing the sample size and lowering the final volume. However, this was not required for this project.

Several solvents such as hexane, acetone, methanol, and ethyl acetate were used in herbicide recovery studies. Because of each herbicide's different solubility, we found that no one solvent would give good recoveries for all chemicals. A mixture of hexane:acetone (60:40) was chosen since it gave relatively good recoveries for all analytes.

The hexane wash in step # 8 is neccessary since it eliminates non polar compounds from the soil.

REFERENCE:

Duc Tran, Residue Analysis Of Atrazine in soil. 1989.

WRITTEN BY: Duc Tran

Dutran

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REVIEWED BY: Catherine Cooper

Catherine Cooper

TITLE: Agricultural Chemist III

APROVED BY: S. Mark Lee

S. Mark Lee

TITLE: Research Agricultural Chemist

APPROVED BY: Terry Jackson

Terry Jackson

TITLE: Quality Assurance Officer

APPENDIX C

Quality Control Data

Table 1. Method Validation Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Simazine
MDL: 0.5 ug/sample

Sample Type: Fallout (Kimble)
Lab: CDFA
Chemist: D. Tran

Lab Sample #	Results (mg)	Spike Level (mg)	Recovery %	$\bar{X}$	SD	CV (%)	LCL	UCL
930	9.70	9.00	108					
	8.89	9.00	98.8					
	9.15	9.00	102					
	8.90	9.00	98.9					
	8.90	9.00	98.9	101	3.97	3.92		
931	16.56	18.0	92.0					
	16.49	18.0	91.6					
	16.56	18.0	92.0					
	17.37	18.0	96.5					
	16.92	18.0	94.1	93	2.1	2.2		
932	21.33	27.0	79.0					
	25.46	27.0	94.3					
	24.87	27.0	92.1					
	27.22	27.0	101					
	27.22	27.0	101	93	9.0	9.6		
			OVERALL:	96	6.6	6.9	76	116

LCL = lower control limit (mean + 3 SD)
UCL = upper control limit (mean - 3 SD)

Table 2. Method Validation Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Diuron
MDL: 0.5 ug/sample

Sample Type: Fallout (Kimble)
Lab: CDFA
Chemist: D. Tran

Lab Sample #	Results (mg)	Spike Level (mg)	Recovery %	$\bar{X}$	SD	CV (%)	LCL	UCL
930	17.28	18.08	95.6					
	16.96	18.08	93.8					
	16.43	18.08	90.9					
	16.16	18.08	89.4					
	16.96	18.08	93.8	93	2.5	2.7		
931	34.91	36.16	96.6					
	33.38	36.16	92.3					
	34.42	36.16	95.2					
	34.93	36.16	96.6					
	34.93	36.16	96.6	95	1.9	2.0		
932	46.10	54.24	85.0					
	49.20	54.24	90.7					
	46.10	54.24	85.0					
	51.58	54.24	95.1					
	51.58	54.24	95.1	90	5.1	5.6		
			OVERALL:	93	3.9	4.2	81	105

LCL = lower control limit (mean + 3 SD)
UCL = upper control limit (mean - 3 SD)

Table 3. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Simazine
MDL: 0.5 ug /sample

Sample Type: Fallout (Kimble)
Lab: CDFA
Chemist: D. Tran

Extraction Set No.'s	Lab Sample #	Results (mg)	Spike Level (mg)	Recovery %	$\bar{X}$	SD	CV (%)
503, 507 -12, 517	1321	14.60	18.00	81.0			
	1320	15.63	18.00	87.0	84	4.2	5.1
501 -2, 504, 508,	1275	17.74	18.00	98.6			
513 - 18	1276	16.12	18.00	89.6	94	6.4	6.8
				OVERALL:	89	7.3	8.2

Table 4. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Diuron
MDL: 0.5 ug /sample

Sample Type: Fallout (Kimble)
Lab: CDFA
Chemist: D. Tran

Extraction Set No.'s	Lab Sample #	Results (mg)	Spike Level (mg)	Recovery %	$\bar{X}$	SD	CV (%)
503, 507 -12, 517	1321	37.50	36.00	104.0			
	1320	39.30	36.00	109.0	107	3.5	3.3
501 -2, 504, 508,	1275	37.68	36.00	104.7			
513 - 18	1276	30.79	36.00	85.5	95	14	14
				OVERALL:	101	10.4	10.4

Table 5. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Simazine
MDL: 0.1 ppb

Sample Type: Water
Lab: CDFA
Chemist: J. White

Extraction Set No.'s	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
601-607	1321	77.23	74.48	104			
608-615	1324	65.02	74.48	87			
	1325	66.18	74.48	89	88	1.4	1.6
616-638	1360	73.90	74.48	99			
	1361	74.80	74.48	101	100	1.41	1.41
641-647	1561	65.00	74.48	87			
	1527	66.00	74.48	88	88	0.7	0.8
651-5, 713-17	3349	76.00	74.48	102			
659-75, 701-3	3496	66.26	74.48	89			
	3497	68.34	74.48	92	91	2.1	2.3
704-12, 720-21	3499	70.19	74.48	94			
	3500	70.05	74.48	94	94	0	0
679-722	3507	74.28	74.48	99			
	3508	74.32	74.48	99	99	0	0
724-30, 737-46	3556	69.31	74.48	93			
	3558	63.95	74.48	86	90	4.9	5.5
650	3689	76.51	74.48	103			
	3690	71.84	74.48	96	100	4.95	4.97
748, 793-97	4050	75.78	74.48	102			
848, 851	5449	69.99	74.48	94			
	5450	71.69	74.48	96	95	1.4	1.5
				OVERALL:	95	5.8	6.1

Table 6. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Diuron
MDL: 0.1 ppb

Sample Type: Water
Lab: CDFA
Chemist: J. White

Extraction Set No.'s	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
601-607	1321	266.7	280.0	95			
608-615	1324	255.0	280.0	91			
	1325	253.0	280.0	90	91	0.7	0.8
616-638	1360	254.0	280.0	91			
	1361	271.0	280.0	97	94	4.2	4.5
641-647	1561	275.0	280.0	98			
	1527	279.0	280.0	99	99	0.7	0.7
651-5, 713-17	3349	293.8	280.0	105			
659-75, 701-3	3496	292.0	280.0	104			
	3497	293.0	280.0	105	105	0.71	0.68
704-12, 720-21	3499	274.0	280.0	98			
	3500	330.0	280.0	118	108	14.14	13.09
679-722	3507	292.0	280.0	104			
	3508	270.0	280.0	96	100	5.66	5.66
724-30, 737-46	3556	266.0	280.0	95			
	3558	278.0	280.0	99	97	2.8	2.9
650	3689	309.0	280.0	110			
	3690	271.0	280.0	97	104	9.19	8.88
748, 793-97	4050	256.0	280.0	91			
848, 851	5449	285.0	280.0	102			
	5450	286.0	280.0	102	102	0.0	0.0
				OVERALL:	99	6.9	6.9

Table 7. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Simazine
MDL: 4 ppb

Sample Type: Soil (clay)
Lab: CDFA
Chemist: B. Fong

Extraction Set No.'s	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\tilde{X}$	SD	CV (%)
1 16	1234	7.7	8.0	96			
	1235	9.8	8.0	122	109	18.4	16.9
17 - 32	1237	8.4	8.0	104			
	1239	9.8	8.0	122			
	1616	12.1	20.0	60.5			
	1617	13.9	20.0	69.5	[illegible]	29	32
45 - 77	1657	15.2	20.0	76.1			
	1661	14.6	20.0	73	75	2.2	2.9
80 - 116	2429	19.6	20.0	97.8			
85 - 98, 106 - 204	3042	23.1	20.0	115.5			
	3043	22.1	20.0	110.5			
	3514	16.5	20.0	82.6			
	3515	18.6	20.0	93.1	100	15.3	15.2
79 - 102	2918	21.7	20.0	108			
	2919	21.7	20.0	108	108	0.0	0.0
220 - 230	5050	20.0	20.0	102.5			
209 - 18, 254	5310	17.6	20.0	85.7			
231 - 41	5341	20.0	20.0	100			
242 - 52	5337	18.5	20.0	90.9			
253, 255 - 64	5504	23.5	20.0	115			
265 - 76	5601	20.5	20.0	100			
277 - 87	5623	20.5	20.0	100			
321 - 334	5650	18.7	20.0	91.7			
				OVERALL:	97	16	17

Table 8. Continuing Quality Control Data (% recvoeries) for the Cal Trans Soil Study.

Study: 104
Analyte: Diuron
MDL: 40 ppb

Sample Type: Soil (clay)
Lab: CDFA
Chemist: B. Fong

Extraction Set No.'s	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1 16	1234	75.0	80.0	94			
	1235	83.0	80.0	103	99	6.4	6.5
17 - 32	1237	94.0	80.0	118			
	1239	83.0	80.0	103			
	1616	158.0	200.0	79			
	1617	128.0	200.0	64	91	24	27
45 - 77	1657	126.0	200.0	63			
	1661	110.0	200.0	55	59	5.7	9.6
80 - 116	2429	185.0	200.0	92.5			
85 - 98, 106 - 204	3042	200.0	200.0	100			
	3043	170.0	200.0	85			
	3514	267.0	200.0	123.1			
	3515	267.0	200.0	123.1	108	18.7	17.3
79 - 102	2918	161.5	200.0	80.7			
	2919	161.5	200.0	80.7	81	0.0	0.0
220 - 230	5050	175.0	200.0	87.6			
209 - 18, 254	5310	186.0	200.0	90.7			
231 - 41	5341	179.0	200.0	88.6			
242 - 52	5337	174.0	200.0	85.4			
253, 255 - 64	5504	201.0	200.0	98.5			
265 - 76	218	149.0	200.0	72.7			
277 - 87	214	146.0	200.0	71.4			
321 - 334	281	230.0	200.0	112.6			
				OVERALL:	90	19	21

Table 9. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Simazine
MDL: 4 ppb

Sample Type: Soil (sandy)
Lab: CDFA
Chemist: B. Fong

Extraction Set No.'s	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1 16	1233	8.4	8.0	104			
	1236	7.7	8.0	96.0	100	5.66	5.66
17 - 32	1238	8.4	8.0	104			
	1240	7.7	8.0	96.0	100	5.66	5.66
	1618	13.6	20.0	68.0			
	1619	16.4	20.0	82.0	75	9.9	13.2
51- 54, 64 - 76	1647	14.8	20.0	74.0			
		13.0	20.0	65.0			
		14.2	20.0	71.0			
		14.8	20.0	74.0	71	4.2	6.0
44 - 78	1991	20.0	20.0	100.0			
		15.0	20.0	75.0			
		18.8	20.0	94.0			
		19.0	20.0	95.2	91	11	12
45 - 58, 63 - 77	1658	14.1	20.0	70.5			
	1656	14.6	20.0	73.0	72	1.8	2.5
80 - 88, 92 - 4	2427	15.7	20.0	78.4			
104	2428	17.4	20.0	86.9			
112, 116	2430	16.0	20.0	80.0			
85 - 6, 90 - 3	3040	20.5	20.0	102.5			
4/7/00	3041	20.7	20.0	103.5			
106 - 7, 113 - 14	3044	21.3	20.0	106.5			
203 - 4	3045	23.3	20.0	116.5			
79, 83 - 4, 89 - 91,	2916	23.0	20.0	115			
95 - 7, 100 -102	2917	20.0	20.0	100			
220 - 230	5051	20.0	20.0	100			
209 - 18, 254	5311	17.2	20.0	85.7			
231 - 241	5342	24.4	20.0	110			
242 - 252	5338	20.0	20.0	100			
253, 255 - 64	5505	18.5	20.0	92.3			
265 - 76	219	20.1	20.0	100			
277 - 87	215	20.1	20.0	100			
321 - 334	282	18.4	20.0	100			
				OVERALL:	91	14	16

Table 10. Continuing Quality Control Data (% recoveries) for the Cal Trans Soil Study.

Study: 104
Analyte: Diuron
MDL: 40 ppb

Sample Type: Soil (sandy)
Lab: CDFA
Chemist: B. Fong

Extraction Set No.'s	Lab Sample #	Results (ppb)	Spike Level (ppb)	Recovery %	$\bar{X}$	SD	CV (%)
1 16	1233	90.0	80.0	112.0			
	1236	98.0	80.0	122.0	117	7.07	6.04
17 - 32	1238	94.0	80.0	118.0			
	1240	75.0	80.0	94.0	106	17.0	16.0
	1618	126.0	200.0	63.0			
	1619	150.0	200.0	75.0	69	8.5	12.3
1- 54, 64 - 7	1647	142.8	200.0	71.4			
		162.9	200.0	81.5			
		145.8	200.0	72.9			
		140.0	200.0	70.0	74	5.2	7.0
44 - 78	1991	172.0	200.0	86.0			
		170.0	200.0	85.0			
		162.0	200.0	81.0			
		164.0	200.0	82.0	84	2.4	2.9
5 - 58, 63 - 7	1658	152.0	200.0	76.0			
	1656	150.0	200.0	75.0	76	0.71	0.94
80 - 88, 92 -	2427	170.0	200.0	84.8			
104	2428	177.0	200.0	88.7			
112, 116	2430	140.0	200.0	70.0			
85 - 6, 90 - 3	3040	191.9	200.0	95.9			
4/7/00	3041	180.0	200.0	90.0			
06 - 7, 113 -	3044	191.8	200.0	95.9			
203 - 4	3045	166.8	200.0	83.4			
, 83 - 4, 89 -	2916	192.3	200.0	96.1			
5 - 7, 100 -10	2917	153.8	200.0	76.9			
220 - 230	5051	192.0	200.0	95.9			
209 - 18, 254	5311	187.0	200.0	93.3			
231 - 241	5342	189.0	200.0	88.5			
242 - 252	5338	189.0	200.0	94.3			
253, 255 - 64	5505	169.0	200.0	84.0			
265 - 76	219	150.0	200.0	75.0			
277 - 87	215	133.0	200.0	66.2			
321 - 334	282	216.0	200.0	107.5			
				OVERALL:	86	14	16

APPENDIX D

Density of Simazine and Diuron Deposited on Kimbies at Sites 1, 2 and 3.

Appendix D Table 1 : **Density of simazine and diuron deposited on Kimbies at Sites 1, 2 and 3.**

Distance from Pavement	Site 1				Site 2				Site 3				Target Density	
	Simazine		Diuron		Simazine		Diuron		Simazine		Diuron		Simazine	Diuron
	mg ft^{-2}													
3' 10"	11.29	25.63	21.55	39.66	14.0	12.0	21.59	18.9	*	19.38	*	25.86	18.76	33.34
9' 6"	2.18	0.97	2.76	1.37	0.40	0.47	0.60	0.59	0.81	0.87	1.07	1.28	0	0
15' 2"	0.08	0.18	0.13	0.32	ND[a]	0.0008	ND	0.0013	0.018	ND	0.025	ND	0	0

* Sample contaminated.
[a] Detection limit = 0.0005 mg/sample for both chemicals.

APPENDIX E

Soil Texture, Organic Carbon and pH Data

Study 104 - Texture, Organic Carbon, and pH results.

Study: 104
Analysis: Texture, Organic Carbon, pH
Report Date: 1/3/92

Sample Type: Soil
Lab: CSUFresno

	Sample No.	Depth	% of Sample >2mm	Texture of portion of Sample <2mm % Sand	% Silt	% Clay	pH	% Organic Carbon
Simulation Site 3	1	1	0.9	16.0	48.0	36.0	6.1	1.2
	2	2	0.1	14.0	44.0	42.0	7.1	0.5
	3	3	0.1	14.0	44.0	42.0	6.7	0.6
	4	4	0.3	16.0	46.0	38.0	6.4	0.8
	5	1	1.5	16.0	50.0	34.0	5.8	1.1
	6	2	0.2	16.0	42.0	42.0	7.7	0.4
	7	3	0.1	14.0	42.0	44.0	6.9	0.6
	8	4	0.4	18.0	44.0	38.0	6.2	0.9
	9	1	0.9	18.0	48.0	34.0	6.4	1.1
	10	2	0.4	16.0	42.0	42.0	7.4	0.4
	11	3	0.6	16.0	42.0	42.0	7.1	0.6
	12	4	2.6	18.0	48.0	34.0	6.8	0.9
Site 2	13	1	16.0	50.0	28.0	22.0	6.5	1.3
	14	2	27.0	48.0	28.0	24.0	6.4	0.9
	15	3	10.8	30.0	42.0	28.0	6.3	0.7
	16	4	0.8	22.0	42.0	36.0	6.6	0.5
	17	1	24.6	48.0	28.0	24.0	5.9	1.3
	18	2	14.3	50.0	28.0	22.0	6.4	0.7
	19	3	1.5	22.0	46.0	32.0	5.9	0.6
	20	4	0	20.0	36.0	44.0	6.9	0.4
	21	1	23.7	50.0	28.0	22.0	5.8	1.6
	22	2	14.5	40.0	32.0	28.0	6.5	0.6
	23	3	4.6	26.0	44.0	30.0	6.2	0.6
	24	4	0	20.0	38.0	42.0	6.6	0.4
Site 1	25	1	51.6	76.0	16.0	8.0	6.6	1.3
	26	2	55.1	80.0	12.0	8.0	7.3	2.6
	27	3	56.9	84.0	10.0	6.0	7.1	8.3
	28	4	60.0	84.0	8.0	8.0	7.1	6.1
	29	1	53.4	78.0	13.0	9.0	6.9	0.8
	30	2	58.5	76.0	15.0	9.0	7.1	2.7
	31	3	62.6	84.0	10.0	6.0	7.2	5.6
	32	4	51.9	86.0	8.0	6.0	7.2	0.5
	33	1	56.8	80.0	10.0	10.0	6.5	0.7
	34	2	62.7	82.0	10.0	8.0	7.1	0.9
	35	3	65.4	86.0	6.0	8.0	7.0	5.4
	36	4	59.6	85.0	7.0	8.0	7.0	2.8
	37	5	56.8	82.0	8.0	10.0	7.0	1.5
	38	6	24.1	44.0	37.0	19.0	6.6	0.8
	39	7	4.5	70.0	18.0	12.0	6.5	0.5
	40	8	64.3	70.0	20.0	10.0	7.0	0.4
	41	9	54.9	92.0	2.0	6.0	7.2	0.2
	42	10	67.8	92.0	4.0	4.0	7.6	0.1
	43	11	73.6	93.0	3.0	4.0	7.8	0.1
	44	1	67.9	78.0	12.0	10.0	7.1	0.6
	45	2	55.5	80.0	12.0	8.0	7.4	0.4

Study 104 - Texture, Organic Carbon, and pH results.

Study: 104
Analysis: Texture, Organic Carbon, pH
Report Date: 1/3/92

Sample Type: Soil
Lab: CSUFresno

	Sample No.	Depth	% of Sample >2mm	Texture of portion of Sample <2mm % Sand	% Silt	% Clay	pH	% Organic Carbon
ite 1	46	3	61.4	84.0	10.0	6.0	7.3	7.0
	47	4	58.6	88.0	7.0	5.0	7.2	7.4
	48	5	64.8	86.0	7.0	7.0	7.2	2.1
	49	6	11.3	64.0	24.0	12.0	6.5	0.6
	50	7	8.0	90.0	4.0	6.0	7.0	0.2
	51	8	49.6	80.0	10.0	10.0	7.1	1.1
	52	9	59.8	87.0	5.0	8.0	7.2	0.9
	53	10	66.1	96.0	0.0	4.0	7.7	0.2
nfiltra-tion Site 4	81	3	0	26.0	37.0	37.0	9.0	1.3
	82	4	0	32.0	38.0	30.0	8.8	0.1
	83	5	0	30.0	43.0	27.0	8.7	0.1
	84	6	0	22.0	40.0	38.0	8.5	0.1
	85	7	0	33.0	28.0	39.0	8.4	0.0
	86	8	0	50.0	20.0	30.0	8.1	0.0
	87	9	0	56.0	16.0	28.0	8.0	0.0
	88	10	0	42.0	30.0	28.0	8.3	0.0
Site 5	91	2	0	28.0	30.0	42.0	6.8	0.0
	92	3	0	26.0	38.0	36.0	7.4	0.3
	93	4	0	40.0	34.0	26.0	7.3	0.1
	94	5	0	74.0	6.0	20.0	6.9	0.1
	95	6	0	80.0	4.0	16.0	6.8	0.1
	96	7	0	82.0	4.0	14.0	6.8	0.1
	97	8	0	83.0	3.0	14.0	6.8	0.1
	98	9	0	70.0	10.0	20.0	7.0	0.1
	99	10	0	70.0	8.0	22.0	7.0	0.1
	100	11	0	78.0	6.0	16.0	7.1	0.1
Site 6	102	2	0	28.0	39.0	33.0	7.5	0.4
	103	3	0	30.0	30.0	40.0	8.5	0.2
	104	4	0	36.0	28.0	36.0	8.2	0.2
	105	5	0	31.0	31.0	38.0	8.1	0.2
	106	6	0	32.0	39.0	29.0	7.9	0.2
	107	7	0	25.0	40.0	35.0	7.8	0.2
	108	8	0	44.0	30.0	26.0	7.8	0.2
	109	9	0	20.0	52.0	28.0	7.9	0.2
	110	10	0	18.0	39.0	43.0	7.8	0.2
Site 7	113	2	11.5	10.0	50.0	40.0	6.4	2.0
	114	3	0	8.0	52.0	40.0	6.9	1.1
	115	4	0	8.0	52.0	40.0	7.5	0.7
	116	5	0	15.0	49.0	36.0	7.9	0.6
	201	6	0	14.0	48.0	38.0	7.9	0.5
	202	7	0	16.0	48.0	36.0	7.9	0.4
	203	8	0	18.0	46.0	36.0	7.9	0.4
	204	9	0	30.0	45.0	25.0	7.8	0.3
	205	10	0	20.0	50.0	30.0	7.7	0.3
	206	11	0	31.0	46.0	23.0	7.7	0.2

APPENDIX F

Raw Data

Study104 - Caltrans Study
Rainfall simulation
SIMAZINE IN RUNOFF WATER

Site=2

	Weeks after application					
	0		2		4	
	Rain		Rain		Rain	
	1	2	1	2	1	2
ug sim in water/liter of water	445.0	336.3	67.8	113.5	109.3	77.1
g sediment/liter water	--	0.7	14.2	0.4	0.3	0.3
ug sim in sed/gram sed	--	4.6	1.0	5.0	1.8	2.3
ug sim in sed/liter water	--	2.9	13.8	1.7	0.5	0.6
ug sim in wat+sed/liter water (SP)	--	339.2	81.6	115.2	109.8	77.7
ug sim in wat+sed/liter water (LL)	--	--	--	141.7	121.3	93.2
Total runoff from plot, liters	21.8	24.2	--	10.5	10.0	21.8
Total ug sim in water in runoff	9701.0	8139.0	--	1191.8	1092.9	1680.4
Total ug sim in sed in runoff	--	69.5	--	18.0	4.7	12.8
Total ug simazine in runoff (SP)	--	8208.5	--	1209.8	1097.6	1693.2
Total ug simazine in runoff (LL)	--	--	--	1488.3	1212.5	2031.0
Measured app rate: mg sim per plot	535.0	535.0	535.0	535.0	535.0	535.0

(CONTINUED)

Study104 - Caltrans Study
Rainfall simulation
SIMAZINE IN RUNOFF WATER

Site=2

	Weeks after application					
	0		2		4	
	Rain		Rain		Rain	
	1	2	1	2	1	2
Sim in wat in runoff as % of appln	1.8	1.5	--	0.2	0.2	0.3
Sim in sed in runoff as % of appln	--	0.0	--	0.0	0.0	0.0
Simazine in runoff as % of appl (SP)	--	1.5	--	0.2	0.2	0.3
Simazine in runoff as % of appl (LL)	--	--	--	0.3	0.2	0.4
Sim in wat in runoff as % of target	1.2	1.0	--	0.2	0.1	0.2
Sim in sed in runoff as % of target	--	0.0	--	0.0	0.0	0.0
Simazine in runoff as % of target (SP)	--	1.0	--	0.2	0.1	0.2
Simazine in runoff as % of target (LL)	--	--	--	0.2	0.2	0.3

Study104 - Caltrans Study
Rainfall simulation
SIMAZINE IN RUNOFF WATER

Site=3

	Weeks after application						
	-1	0		2		4	
	Rain	Rain		Rain		Rain	
	1	1	2	1	2	1	2
ug sim in water/liter of water	5.2	565.0	266.0	327.2	151.9	239.8	198.3
g sediment/liter water	0.1	--	2.6	3.1	0.5	0.7	0.9
ug sim in sed/gram sed	0.4	--	3.5	2.3	3.1	5.1	3.0
ug sim in sed/liter water	0.0	--	9.1	7.1	1.6	3.4	2.6
ug sim in wat+sed/liter water (SP)	5.2	--	275.1	334.3	153.5	243.2	200.9
ug sim in wat+sed/liter water (LL)	7.7	--	--	--	204.2	276.7	198.9
Total runoff from plot, liters	44.4	32.5	57.4	45.5	90.0	64.5	65.0
Total ug sim in water in runoff	224.6	18362.5	15268.1	14889.6	13672.9	15468.3	12889.4
Total ug sim in sed in runoff	1.6	--	522.0	321.9	141.6	218.9	167.7
Total ug simazine in runoff (SP)	226.2	--	15790.2	15211.5	13814.4	15687.2	13057.1
Total ug simazine in runoff (LL)	331.0	--	--	--	18377.7	17845.0	12925.6
Measured app rate: mg sim per plot	--	802.0	802.0	802.0	802.0	802.0	802.0

(CONTINUED)

Study104 - Caltrans Study
Rainfall simulation
SIMAZINE IN RUNOFF WATER

Site=3

	Weeks after application						
	-1	0		2		4	
	Rain	Rain		Rain		Rain	
	1	1	2	1	2	1	2
Sim in wat in runoff as % of appln	--	2.3	1.9	1.9	1.7	1.9	1.6
Sim in sed in runoff as % of appln	--	--	0.1	0.0	0.0	0.0	0.0
Simazine in runoff as % of appl (SP)	--	--	2.0	1.9	1.7	2.0	1.6
Simazine in runoff as % of appl (LL)	--	--	--	--	2.3	2.2	1.6
Sim in wat in runoff as % of target	0.0	2.3	1.9	1.9	1.7	2.0	1.6
Sim in sed in runoff as % of target	0.0	--	0.1	0.0	0.0	0.0	0.0
Simazine in runoff as % of target (SP)	0.0	--	2.0	1.9	1.8	2.0	1.7
Simazine in runoff as % of target (LL)	0.0	--	--	--	2.3	2.3	1.6

Study104 - Caltrans Study
Rainfall simulation
SIMAZINE IN RUNOFF WATER

Site=3

	Weeks after application						
	-1	0		2		4	
	Rain	Rain		Rain		Rain	
	1	1	2	1	2	1	2
ug sim in water/liter of water	5.2	565.0	266.0	327.2	151.9	239.8	198.3
g sediment/liter water	0.1	--	2.6	3.1	0.5	0.7	0.9
ug sim in sed/gram sed	0.4	--	3.5	2.3	3.1	5.1	3.0
ug sim in sed/liter water	0.0	--	9.1	7.1	1.6	3.4	2.6
ug sim in wat+sed/liter water (SP)	5.2	--	275.1	334.3	153.5	243.2	200.9
ug sim in wat+sed/liter water (LL)	7.7	--	--	--	204.2	276.7	198.9
Total runoff from plot, liters	44.4	32.5	57.4	45.5	90.0	64.5	65.0
Total ug sim in water in runoff	224.6	18362.5	15268.1	14889.6	13672.9	15468.3	12889.4
Total ug sim in sed in runoff	1.6	--	522.0	321.9	41.6	218.9	167.7
Total ug simazine in runoff (SP)	226.2	--	15790.2	15211.5	13814.4	15687.2	13057.1
Total ug simazine in runoff (LL)	331.0	--	--	--	18377.7	17845.0	12925.6
Measured app rate: mg sim per plot	--	802.0	802.0	802.0	802.0	802.0	802.0

(CONTINUED)

Study 104 - Caltrans Study
Rainfall simulation
DIURON IN RUNOFF WATER

Site=2

	Weeks after application					
	0		2		4	
	Rain		Rain		Rain	
	1	2	1	2	1	2
Diur in wat in runoff as % of appln	3.1	1.9	--	0.3	0.2	0.4
Diur in sed in runoff as % of appln	--	0.0	--	0.0	0.0	0.0
Diuron in runoff as % of appl (SP)	--	1.9	--	0.3	0.2	0.4
Diuron in runoff as % of appl (LL)	--	--	--	0.3	0.2	0.4
Diur in wat in runoff as % of target	1.8	1.1	--	0.2	0.1	0.3
Diur in sed in runoff as % of target	--	0.0	--	0.0	0.0	0.0
Diuron in runoff as % of target (SP)	--	1.1	--	0.2	0.1	0.3
Diuron in runoff as % of target (LL)	--	--	--	0.2	0.1	0.2
mg diur in runoff/mile of highway	--	11515.6	--	1678.4	1084.3	2671.7

Study 104 - Caltrans Study
Rainfall simulation
DIURON IN RUNOFF WATER

Site=2

	Weeks after application					
	0		2		4	
	Rain		Rain		Rain	
	1	2	1	2	1	2
Diur in wat in runoff as % of appln	3.1	1.9	--	0.3	0.2	0.4
Diur in sed in runoff as % of appln	--	0.0	--	0.0	0.0	0.0
Diuron in runoff as % of appl (SP)	--	1.9	--	0.3	0.2	0.4
Diuron in runoff as % of appl (LL)	--	--	--	0.3	0.2	0.4
Diur in wat in runoff as % of target	1.8	1.1	--	0.2	0.1	0.3
Diur in sed in runoff as % of target	--	0.0	--	0.0	0.0	0.0
Diuron in runoff as % of target (SP)	--	1.1	--	0.2	0.1	0.3
Diuron in runoff as % of target (LL)	--	--	--	0.2	0.1	0.2
mg diur in runoff/mile of highway	--	11515.6	--	1678.4	1084.3	2671.7

Study 104 - Caltrans Study
Rainfall simulation
DIURON IN RUNOFF WATER

Site=3

	Weeks after application						
	-1	0		2		4	
	Rain	Rain		Rain		Rain	
	1	1	2	1	2	1	2
ug diur in water/liter of water	12.8	1750.0	592.4	1064.8	344.8	769.8	415.1
g sediment/liter water	0.1	--	2.6	3.1	0.5	0.7	0.9
ug diur in sed/gram sed	0.4	--	7.0	10.4	5.8	10.1	5.0
ug diur in sed/liter water	0.0	--	18.4	31.8	2.9	6.7	4.3
ug diur in wat+sed/liter water (SP)	12.8	--	610.8	1096.6	347.7	776.5	419.4
ug diur in wat+sed/liter water (LL)	12.6	--	--	--	383.0	779.1	375.8
Total runoff from plot, liters	44.4	32.5	57.4	45.5	90.0	64.5	65.0
Total ug diuron in wat in runoff	552.7	56875.0	34001.8	48448.7	31028.3	49650.4	26980.7
Total ug diuron in sed in runoff	1.6	--	1057.2	1446.5	264.1	434.6	278.2
Total ug diuron in runoff (SP)	554.3	--	35059.0	49895.2	31292.4	50085.0	27258.9
Total ug diuron in runoff (LL)	543.3	--	--	--	34468.5	50250.1	24427.9
Measured app rate: mg diur per plot	--	1073.0	1073.0	1073.0	1073.0	1073.0	1073.0

(CONTINUED)

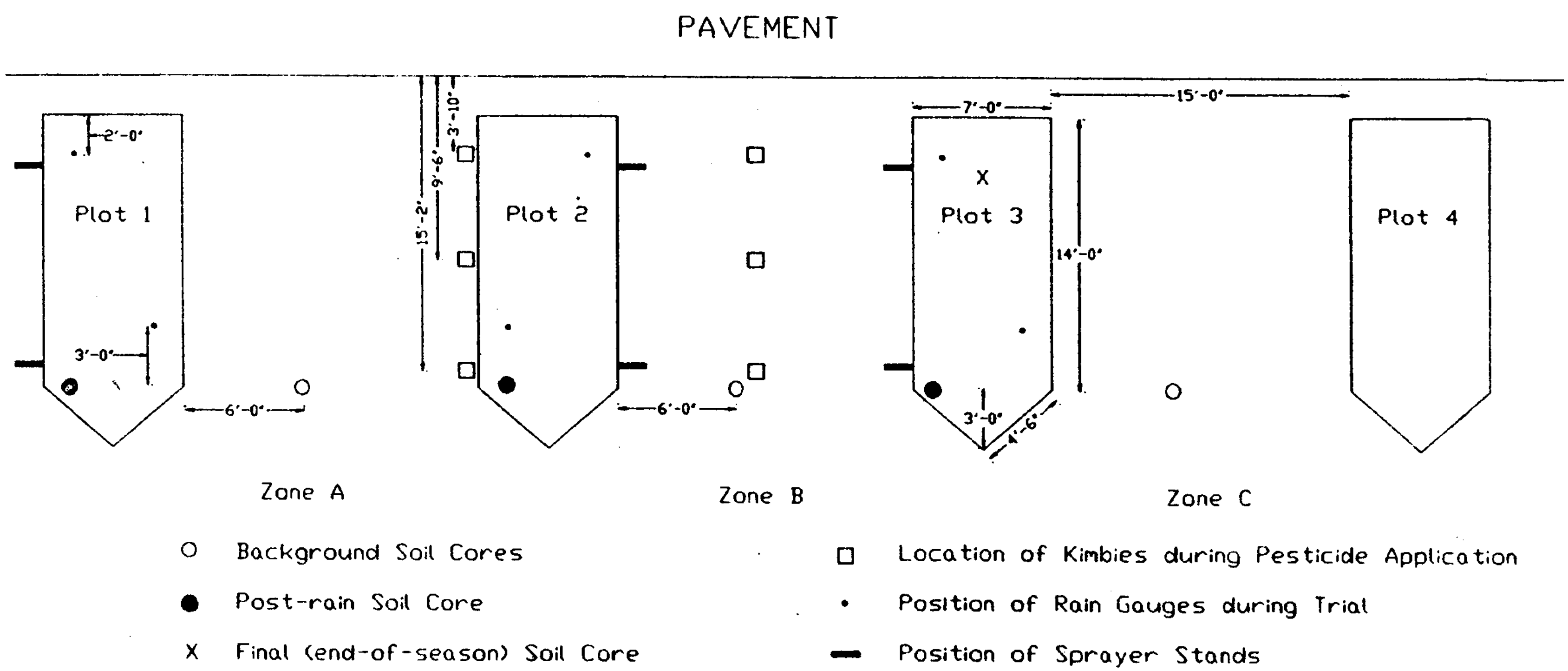
Study 104 - Caltrans Study
Rainfall simulation
DIURON IN RUNOFF WATER

Site=3

	Weeks after application						
	-1	0		2		4	
	Rain	Rain		Rain		Rain	
	1	1	2	1	2	1	2
Diur in wat in runoff as % of appln	--	5.3	3.2	4.5	2.9	4.6	2.5
Diur in sed in runoff as % of appln	--	--	0.1	0.1	0.0	0.0	0.0
Diuron in runoff as % of appl (SP)	--	--	3.3	4.7	2.9	4.7	2.5
Diuron in runoff as % of appl (LL)	--	--	--	--	3.2	4.7	2.3
Diur in wat in runoff as % of target	0.0	4.1	2.4	3.5	2.2	3.5	1.9
Diur in sed in runoff as % of target	0.0	--	0.1	0.1	0.0	0.0	0.0
Diuron in runoff as % of target (SP)	0.0	--	2.5	3.6	2.2	3.6	1.9
Diuron in runoff as % of target (LL)	0.0	--	--	--	2.5	3.6	1.7
mg diur in runoff/mile of highway	417.9	--	26434.5	37621.0	23594.5	37764.1	20553.2

APPENDIX G

Site Diagram (Fig. 4) in Feet and Inches


PAVEMENT
2'-0"
3'-10"
9'-6"
15'-2"
7'-0"
15'-0"
Plot 1
Plot 2
Plot 3
Plot 4
X
14'-0"
3'-0"
6'-0"
6'-0"
3'-0"
4'-6"
Zone A
Zone B
Zone C
Background Soil Cores
Post-rain Soil Core
X Final (end-of-season) Soil Core
Location of Kimbies during Pesticide Application
Position of Rain Gauges during Trial
Position of Sprayer Stands